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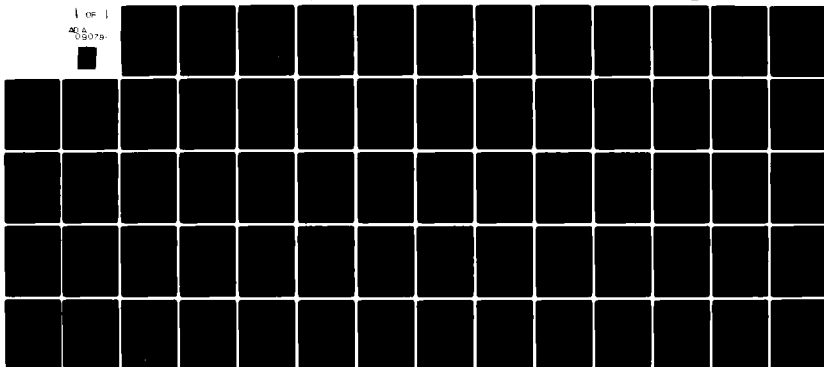
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Part one of this report deals with attempts over the past several years to devise a more sophisticated theory of diffusion controlled reactions than that presented by Collins and Kimball. In particular, the investigators were interested in a more realistic formulation of the problem of high concentration quenching where quenches in the vicinity of the molecule to be quenched must be considered. It was desired however, to obtain a formalism which was tractable mathematically and		

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20. ABSTRACT CONTINUED

which contained parameters which would be related to experiment. Part two deals with the photophysics of systems exhibiting molecular association both in the ground and excited states has been studied. The emphasis has been on kinetic models, the measurement of rate constants associated with these models, and the determination of activation parameters and equilibrium thermodynamic parameters associated with the exciplex formation and disappearance. Studies of solvent effects and steric effects on the behaviour of exciplex systems have been carried out. The case of rapid equilibrium where the monomer and exciplex decay with the same rate constant has also been examined.



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SECTION I

INFLUENCE OF DIFFUSION ON FLUORESCENCE

QUENCHING.

This section deals with our attempts over the past several years to devise a more sophisticated theory of diffusion controlled reactions than that presented by Collins and Kimball. In particular, we were interested in a more realistic formulation of the problem of high concentration quenching where quenches in the vicinity of the molecule to be quenched must be considered. It was desired however, to obtain a formalism which was tractable mathematically and which contained parameters which would be related to experiment.

1. SOME HISTORY

Early interest in diffusion controlled processes centred around the coagulation of colloidal particles. These particles were large enough that the solvent provided an almost perfect continuum for diffusion. Fick's laws were invoked and concentration independent diffusion coefficients employed. It was assumed that one could use a mutual diffusion coefficient ($D_A + D_Q$) to describe diffusion in a system where only D or Q was allowed to move.

Smoluchowski¹ in 1917 published a paper describing the solution to Fick's second law for reactions occurring with 100% efficiency upon each encounter. Collins and Kimball² modified this approach to take into account the possibility of non-productive encounters. Their work was in part stimulated by a paper by Sveshnikoff³ which improperly treated this problem of inefficiency.

Noyes⁴ in a series of papers in the 60's examined the problem from the point of view of pair diffusion with essentially the same results. Noyes' analysis provides valuable insight into the origin of the phenomenon.

Others active in this field were Waite,⁵ Weller,⁶ La Mer and Umlberger,⁷ and Yguerabidi, Dillon and Burton.⁸

In 1973, Fixman and Wilemski⁹ described a more general approach to the problem. Recently, Andre, Niclaude and Ware¹⁰ starting with Fixman-Wilemski equation have attempted to develop more realistic models for diffusion controlled and partially diffusion controlled reactions.

In spite of all this theoretical work, very little experimental work has been published which provides laboratory verification to the equations which are in common use for correcting for transient effects in diffusion controlled processes. Ware and Novros¹¹ and Ware and Nemzek¹² studied systems where the non-exponential decay could be subjected to quantitative analysis and a comparison made between transient and steady-state quenching. Work in the author's laboratory in collaboration with J.C. Andre, M. Bouchy and M. Niclaude¹³ has recently resulted in additional experimental work and the re-analysis of some of the data from earlier work. However, the integrated theoretical output still exceeds experimental work in this field by a wide margin.

2. SIMPLE THEORY

Smoluchowski¹ solved Fick's second law

$$\frac{\partial c}{\partial t} = D_{AB} \nabla^2 c \quad (1)$$

for the case where one particle is fixed at the origin and the other particle moves with diffusion coefficient D_{AB} . c is the concentration of the diffusing species, in molecules per cm^3 , and for radial diffusion

$$\nabla^2 = \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) \quad (2)$$

Smoluchowski considered every encounter between particles to result in reaction and therefore used the boundary conditions

$$c(r,0) = c_0, \quad c(\infty,t) = c_0, \quad c(\sigma,t) = 0 \quad (3)$$

where c_0 is the initial concentration of the diffusing species, r is the distance from the origin, and σ is the sum of the radii of the two particles.

The solution to Eq. (2) with these boundary conditions is

$$c(r,t) = c_0 \left(1 - \frac{\sigma}{r} \operatorname{erfc} \left(\frac{(r - \sigma)}{\sqrt{4D_{AB}t}} \right) \right) \quad (4)$$

where

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-z^2} dz$$

The flux at time t , through the sphere of radius σ around the origin, is

$$\Phi = 4\pi\sigma^2 D_{AB} \left(\frac{\partial c(r,t)}{\partial r} \right)_{r=\sigma} \quad (5)$$

Taking the derivative of Eq. (4), one obtains

$$\Phi = 4\pi\sigma D_{AB} c_0 \left(1 + \frac{\sigma}{\sqrt{\pi D_{AB}t}} \right) \quad (6)$$

The observed rate constant is thus

$$k(t) = \frac{\Phi}{C_0} = 4\pi\sigma D_{AB} N' \left(1 + \frac{\sigma}{\sqrt{\pi D_{AB}t}} \right) \quad (7)$$

where C_0 is now expressed in moles per liter, and N' is Avogadro's number divided by 1000.

Collins and Kimble² pointed out that the equations derived by Smoluchowski contained certain disturbing features. Firstly, at $t = 0$, the flux as given by Eq. (6) was infinite. Secondly, the theory made no provision for cases wherein the probability of reaction on encounter was less than unity. Sveshnikoff³ had attempted to correct for this second point by multiplying the flux by a factor, α , less than unity. Collins and Kimble showed that this procedure was incorrect since it implied that the flux differed from the decrease in the total amount of the diffusing species.

Collins and Kimble eliminated these difficulties by allowing for the possibility that not every particle reacted on reaching distance σ from the origin. This was done by assuming that the rate of reaction was proportional to the probability that the diffusing particle was between σ and $(\sigma + d\sigma)$. That is,

$$\Phi = \kappa 4\pi \sigma^2 c(\sigma,t) \quad (8)$$

where κ is some rate constant. Since the flux is also given by Eq. (5), one obtains the condition

$$c(\sigma, t) = \frac{D_{AB}}{\kappa} \left(\frac{\partial c(r, t)}{\partial r} \right)_{r=\sigma} \quad (9)$$

This is known as the "radiation boundary condition", due to its use in heat conduction problems. Eq. (1) is now solved with the boundary conditions

$$\begin{aligned} c(r, 0) &= c_0 \\ c(\infty, t) &= c_0 \end{aligned} \quad (10)$$

$$c(\sigma, t) = \frac{D_{AB}}{\kappa} \left(\frac{\partial c(r, t)}{\partial r} \right)_{r=\sigma}$$

The solution with these boundary conditions is well known,

$$\begin{aligned} c(r, t) = c_0 \left\{ 1 - \frac{\sigma - b}{r} \left[\operatorname{erfc} \left(\frac{r - \sigma}{\sqrt{4D_{AB}t}} \right) \right. \right. \\ \left. \left. - \exp \left(\frac{D_{AB}t}{\xi^2} + \frac{r - \sigma}{\xi} \right) \operatorname{erfc} \left(\frac{\sqrt{D_{AB}t}}{\xi} + \frac{r - \sigma}{\sqrt{4D_{AB}t}} \right) \right] \right\} \end{aligned} \quad (11)$$

where

$$\xi = \frac{\sigma D_{AB}}{D_{AB} + \kappa \sigma} \quad (12)$$

Using Eq. (8) and setting r equal to σ in Eq. (11), one obtains for the flux

$$\phi = \frac{4\pi\sigma D_{AB}c_0}{1 + \frac{D_{AB}}{\kappa\sigma}} \left[1 + \frac{\kappa\sigma}{D_{AB}} e^{x^2} \operatorname{erfc}(x) \right] \quad (13)$$

where

$$x = \frac{\sqrt{D_{AB}t}}{\beta} \quad (14)$$

For $x > 1$, one may use the asymptotic expression for $\text{erfc}(x)$

$$e^{-x^2} = \text{erfc}(x) = \frac{1}{x\sqrt{\pi}} \left(1 - \frac{1}{2x^2} + \frac{3}{4x^4} - \frac{15}{8x^6} + \dots \right) \quad (15)$$

The error involved in truncating this expansion is less than the value of the first neglected term. For ordinary values of κ , D_{AB} , and σ , as will be shown later, the term $(1/2x^2)$ is equal to 0.01 in approximately 10^{-10} sec. Thus, all but the first term in the expansion can be neglected, and

$$e^{-x^2} \text{erfc}(x) = \frac{1}{x\sqrt{\pi}} \quad (16)$$

The flux then becomes

$$\Phi = 4\pi D_{AB} \bar{\sigma} c_o \left(1 + \frac{\bar{\sigma}}{\sqrt{\pi D_{AB} t}} \right) \quad (17)$$

where

$$\bar{\sigma} = \frac{\sigma}{1 + \left(\frac{D_{AB}}{\kappa \sigma} \right)} \quad (18)$$

The time dependent rate constant, $k(t)$, is then given by

$$k(t) = \frac{\Phi}{c_o} = 4\pi D_{AB} \bar{\sigma} N' \left(1 + \frac{\bar{\sigma}}{\sqrt{\pi D_{AB} t}} \right) \quad (19)$$

This equation is of the same form as Smoluchowski's equation, Eq. (7), except that σ has been replaced by $\bar{\sigma}$.

It is of interest to examine the flux as the time approaches zero. For small values of t , one cannot use the asymptotic expansion of $\text{erfc}(x)$, but instead must integrate the Taylor's series expansion of e^{-x^2} to obtain

$$\text{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-x^2} dx = 1 - \frac{2x}{\sqrt{\pi}} \left(1 - \frac{x^2}{(3)1!} + \frac{x^4}{(5)2!} - \dots \right) \quad (20)$$

On multiplying this expression by the Taylor's series expansion of e^{-x^2} , one finds that the flux at small t is given by

$$\Phi = \frac{4\pi\sigma D_{AB}^C c_0}{1 + \frac{D_{AB}}{\kappa\sigma}} \left[1 + \frac{\kappa\sigma}{D_{AB}} \left(1 - \frac{2}{\sqrt{\pi}} \sqrt{\frac{D_{AB}t}{\pi}} + \dots \right) \right] \quad (21)$$

The flux as given by this equation is finite as t approaches 0. At $t = 0$, the flux is equal to $4\pi\sigma^2\kappa c_0$.

Eq. (19) is the basic equation which is used in the analysis of the fluorescence quenching data. The derivation of this equation depends critically on the validity of truncating the asymptotic expansion of $e^{x^2} \operatorname{erfc}(x)$. This truncation neglects the term $(2x^2)^{-1}$ where

$$x = \frac{(D_{AB} + \kappa\sigma)}{\sigma D_{AB}} \sqrt{D_{AB}t} \quad (22)$$

In order to truncate the expansion in this fashion, $(2x^2)^{-1}$ must be much less than unity. It is desirable to determine the range of σ , D_{AB} , and t over which Eq. (19) can be used. To do this, one must estimate the value of κ , and then calculate values of $(2x^2)^{-1}$ for given σ , D_{AB} , and t .

As can be seen from Eq. (8), κ has the units of cm sec^{-1} . Noyes⁴ assumed that one can relate κ to the rate constant, k_g , calculated from the kinetic theory of gases, using the relation

$$\kappa_g = 4\pi\sigma^2\kappa \quad (23)$$

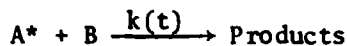
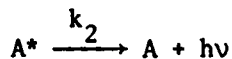
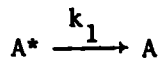
where κ_g is on the order of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. Let us take $5 \times 10^{-8} \text{ cm}$ as a reasonable estimate of σ . Then in non-viscous media, with $D_{AB} = 5 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, x is equal to $5.9 \times 10^5 \sqrt{t}$. When t is 10 psec, $(2x^2)^{-1}$ is found to be 0.14, which is not negligible compared to unity. When t is 100 psec, $(2x^2)^{-1}$ is equal to 0.014, which is small compared to unity.

In more viscous media, with $D = 5 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$, x is equal to $1.47 \times 10^6 \sqrt{t}$. When t is 10 psec, $(2x^2)^{-1}$ is 0.023. When t is 100 psec, $(2x^2)^{-1}$ is 0.0023.

It is thus apparent, that even if the estimate of κ is only approximately correct, the truncation of the expansion is valid for nsec time scales in viscous media.

3. APPLICATION TO FLUORESCENCE QUENCHING

Consider the following fluorescence reaction mechanism:



The rate constant $k(t)$ is given by Eq. (19), and $(k_1 + k_2)^{-1}$ is equal to τ_0 , the unquenched lifetime of the system. For δ -pulse excitation

$$\frac{d[A^*]}{dt} = [A^*] \left(-\frac{1}{\tau_0} - k(t)[B] \right) \quad (24)$$

When the concentration of B is much larger than $[A^*]_0$, then B can be considered to be time independent, and

$$\frac{[A^*]}{[A^*]_0} = \exp(-at - 2b\sqrt{t}) \quad (25)$$

where $[A^*]_0$ is the concentration of A^* at time 0, and

$$a = \frac{1}{\tau_0} + 4\pi\bar{\sigma} D_{AQ} N' [B] \quad (26)$$

$$b = 4\sqrt{\pi D_{AQ}} \bar{\sigma}^2 N' [B] \quad (27)$$

The decay law, $G(t)$, is predicted to be

$$G(t) = \exp(-at - 2b\sqrt{t}) \quad (28)$$

The response of the system under steady state illumination is obtained by considering excitation by a step function F_0 . If the number of excited molecules of A is given by $n_A(t)$, we have that

$$n_A(t) = \int_0^t F(t - t') G(t') dt' = F_0 \int_0^t G(t') dt'$$

when $F(t)$ is a step function. On obtaining an expression for $n_A(t)$, one then lets $t \rightarrow \infty$ in order to arrive at the number of molecules, $n_A(\infty)$, in the steady state.

The result is¹²

$$\frac{I_o}{I} = \frac{n_A^{(\infty)}_{B=0}}{n_A^{(\infty)}} = \frac{(1 + 4\pi\bar{\sigma}D_{AQ}N'[B]\tau_o)}{1 - b\sqrt{\frac{\pi}{a}} \exp\left(\frac{b^2}{a}\right) \operatorname{erfc}\left(\frac{b}{\sqrt{a}}\right)} \quad (29)$$

This expression may be used for analysis of steady state data obtained under conditions where the time dependence of the rate constant is expected to be important.

Eqs. (28) and (29) are frequently used for the analysis of diffusion controlled reactions.

Experimental studies of the validity of Eqs. (28) and (29) indicate the following:^{11,12,14,15}

(a) $\bar{\sigma}$ is always greater than the collisional distance σ .

(b) Calculated values of $\bar{\sigma}$ from steady state measurements are greater than values of $\bar{\sigma}$ from decay law analysis; with dramatic departures in some cases, of the Stern-Volmer plot from that predicted from the decay law parameters.

4. AN IMPROVED MODEL

A more realistic, but still simple model, has recently been proposed by Andre, Niclaus and Ware.¹⁰

Theoretically, it is possible to determine variations of apparent rate constant of reaction $k_a(t)$ versus time by resolution of the classical equation of Wilemski and Fixman:⁹

$$\partial\phi(r,t)/\partial t + \xi\phi(r,t) = -k(r)\phi(r,t), \quad (30)$$

where $\phi(r,t)$ is the ratio of the configuration distribution function of the molecules B to the mean concentration of B, ξ is a time evolution operator relating to the diffusion process¹⁶

$$\xi x \equiv -D\nabla^2 x + K\nabla\psi \cdot \nabla x + K\nabla^2\psi x, \quad (31)$$

with: ψ the electrical potential around the molecule A^* , K a mobility coefficient.

$k(r)$ is a rate constant (expressed in s^{-1}) of reaction of an A^* molecule with a B molecule at the distance r .

The analytical or numerical variations of $k(r)$ versus r have not

been reported in the literature (except for Förster energy transfer).¹⁷ Except in the case of chemical reaction between ions, the value of Ψ is not known. However, one can assume that, in the case of uncharged molecules, Ψ takes a significant value only for values of r near of σ .¹⁸

The model of Andre, Niclaude and Ware is a diffusion model consisting of two distinct volumes in the reacting system centered on a molecule A^* towards which molecules B diffuse:

(i) a reaction range between σ and σ' wherein the chemical reaction occurs with a chemical rate constant practically infinite; we assume that no diffusion occurs in this range, i.e., $\phi(r,t) = 0$ for $r \in [\sigma, \sigma']$,

(ii) an external volume ($r > \sigma'$) in which no chemical reaction but only diffusion occurs.

Then, we have to solve the following system:

for $r \in [\sigma, \sigma']$ and $t > 0$

$$\phi(r,t) = 0;$$

for $r > \sigma'$

$$\partial\phi(r,t)/\partial t + \mathcal{L}\phi(r,t) = 0,$$

with

$$\mathcal{L}\phi(r,t) \equiv -D\nabla^2\phi(r,t). \quad (32)$$

Under these conditions, the value of the apparent rate constant is given:^{1,19}

$$k_a(t) = 4\pi N\sigma'D[\partial\phi(r,t)/\partial r]_{\sigma'},$$

which becomes

$$k_a(t) = k_0[1 + \sigma'(\pi Dt)^{-1/2}], \quad (33)$$

where $k_0 = 4\pi N\sigma'D$.

If A^* is a singlet excited state, one can measure the intensity of fluorescence of A^* in the presence (I) or in the absence (I_0) of B, all other experimental conditions being constant.

Theoretically, one determines the variations of I with concentration [B] taking into account that for $t = 0$, there is a probability P

of finding a molecule B inside the chemical reaction volume V_1 [$V_1 = 4/3 \pi(\sigma'^3 - \sigma^3)$]. Then one can postulate

(i) practically instantaneous deactivation of A^* having at least one B molecule in V_1 ,

(ii) deactivation from B molecules reaching σ' after diffusion (Smoluchowski).

All other conditions being constant, for the steady-state experiment, the ratio of I_0 over I can be expressed by:

$$\frac{I_0}{I} = \frac{\int_0^\infty (A^*)_{[B]=0} dt}{\int_0^\infty (A^*)_{[B] \neq 0} dt}. \quad (34)$$

On the contrary, by flash excitation where one measures the relative variations of A^* versus time, only dynamic quenching will be observed.

The generalized distribution of Smoluchowski²⁰ gives the probability of having a given distribution of B molecules between σ and σ' around A^* .

If $[B]$ is the average concentration of B, N the Avogadro's number, the probability $P(n)$ to have n molecules B in V_1 is:

$$P(n) = e^{-NV_1[B]} \frac{(NV_1[B])^n}{n!}, \quad (35)$$

or

$$P(n) = e^{-w} \frac{w^n}{n!}$$

with

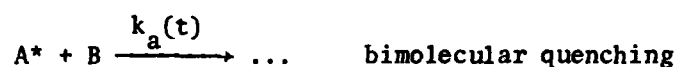
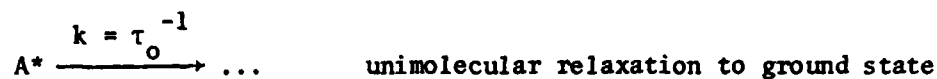
$$w = NV_1[B].$$

The probability P to have at least one B in V_1 is expressed by:

$$P = \sum_{i=1}^{\infty} e^{-w} \frac{w^i}{i!} = 1 - e^{-w}.$$

Then, if $(A)_0$ molecules are excited at $t = 0$, we obtain $(A)_0 e^{-NV_1[B]}$ excited molecules after this very fast deactivation process.

The following scheme for the disappearance of A^* can be used



then

$$d(A^*)/dt = - [k + k_a(t)[B]](A^*)$$

leading to

$$(A^*)(t) = (A^*)_0 \exp[-NV_1[B]] \times \exp\{-[k + k_0[B] + 2\sigma'(\pi Dt)^{-1/2}k_0[B]]t\}, \quad (36)$$

and

$$\frac{I_0}{I} = \frac{\exp[NV_1[B]] \int_0^\infty \exp(-kt) dt}{\int_0^\infty \exp\{-[k + k_0[B] + 2\sigma'(\pi Dt)^{-1/2}k_0[B]]t\} dt} \quad (37)$$

then

$$\frac{I_0}{I} = \frac{e^{NV_1[B]}}{I(\lambda)} [1 + k_0\tau[B]], \quad (38)$$

where

$$\lambda = \frac{2}{\pi^{1/2}} \frac{k_0\tau_0[B]}{[1 + k_0\tau_0[B]]^{1/2}} \frac{\sigma'}{(D\tau_0)^{1/2}},$$

and

$$I(\lambda) = \int_0^\infty \exp(-u - \lambda u^{1/2}) du$$

$$= 1 - \frac{1}{2} \lambda \pi^{\frac{1}{2}} \exp\left(\frac{1}{4} \lambda^2\right) \text{Erfc}\left(\frac{1}{2} \lambda\right).$$

Then, by flash excitation, one measures the relative variations of $(A^*)(t)$ (Eq. (36)) due to unimolecular relaxation and to the reaction of A^* and B molecules reaching σ' (the true transient effect occurs in $\sigma'(\pi Dt)^{-\frac{1}{2}}$). On the contrary, by steady-state measurement, one other effect, due to the reaction of A^* with B presents in V_1 is superimposed on the other (apparent transient effect due to $e^{NV_1[B]}$).

For small quencher concentrations, the first and the second terms of the Taylor series of I_0/I versus $[B]$ are:

$$\frac{I_0}{I} = 1 + \{NV_1 + k_0 \tau_0 [1 + \sigma' (D\tau_0)^{-\frac{1}{2}}]\} [B] + \dots \quad (39)$$

All other terms in this expansion can be neglected. Then, the apparent constant of quenching K_{SV} is equal to:

$$K_{SV} = NV_1 + k_0 \tau_0 [(1 + \sigma' (D\tau_0)^{-\frac{1}{2}})]. \quad (40)$$

For most of the studies which are reported, values of σ' around 10 Å (+1) were obtained (for example, refs. 11,12,14,15). But, the calculated collision value is always around 6 Å. Then, under these conditions, the importance of NV_1 is about $NV_1 \approx 1 \text{ mole}^{-1} \text{ l.}$

For low viscosity solutions and for excited molecules with lifetimes greater than 10 ns, one can neglect this static effect. On the contrary, in order to observe transient effects, one needs a value of $\sigma' (D\tau_0)^{-\frac{1}{2}}$ as great as possible which can be obtained by lowering D (or increasing viscosity η) and by decreasing k_0 , i.e., by increasing relative importance of static quenching term (see Eqs. (38) and (39)).

5. A HIGHER LEVEL OF SOPHISTICATION

A more rigorous theory, but one that still yields relatively simple equations, has been developed by Andre, Bouchy, Niclaude and Ware.¹³

One again starts with

$$\frac{\partial \phi(r,t)}{\partial t} + \mathcal{L} \phi(r,t) = -k(r) \cdot \phi(r,t) \quad (30)$$

Knowing \mathcal{L} and $k(r)$, it is possible to determine the variation of $\phi(r,t)$ with t , by using the Laplace transform or numerical tech-

niques.¹³ The apparent rate constant is given in $M^{-1} \cdot \text{sec}^{-1}$ by the expression

$$k_a(t) = \int_{\sigma}^{\sigma'} 4\pi r^2 N k(r) \phi(r,t) dr$$

In the case where a chemical reaction occurs, the variation of $k(r)$ is not well known and a simplified model must still be employed. Reaction or interaction between molecules requires the overlap of the external molecular orbitals of the two molecules. The value of the overlap of molecular orbitals is known; it is a decreasing function of r and, beyond a value of r of some \AA , there is practically no overlap.

In our model, we take $k(r)$ to be practically constant and equal to some value K for distances smaller than σ' , i.e., for $\sigma < r < \sigma'$. At distances greater than σ' , $k(r)$ is set equal to zero. Thus, the equation for $K_a(t)$ becomes

$$K_a(t) = 4\pi N k \int_{\sigma}^{\sigma'} \phi(r,t) r^2 dr \quad (41)$$

We have proposed a diffusion model considering of two distinct volumes in the reacting system centered on a molecule A toward which molecules B diffuse:

- a reaction zone consisting of the volume between a sphere of radius σ' and a sphere of radius σ wherein the chemical reaction occurs with a rate constant k ; we assume that no diffusion occurs in this range, i.e., $\phi(r,t)$ is independent of r .
- an external volume ($r > \sigma'$) in which no chemical reaction but only diffusion occurs.

The value of σ' and the rate constant k are determined by the variation of ψ and by the particular value $k(r)$ in the vicinity to the molecule A. The model is illustrated in Fig. 1.

For $r \geq \sigma'$, taking $\psi = 0$ for uncharged particles,

$$\frac{\partial \phi}{\partial t} = D \nabla^2 \phi = D \left[\frac{\partial^2 \phi}{\partial r^2} + \frac{2}{r} \frac{\partial \phi}{\partial r} \right] \quad (42)$$

For $\sigma \leq r < \sigma'$, the flow of molecules B at the distance σ' of A has to be equal to both the accumulation of B inside the reaction

volume and the disappearance of B in the chemical reaction $A + B \rightarrow C$. Thus, we must have

$$4\pi N\sigma'^2 D \left(\frac{\partial \phi}{\partial r} \right)_{\sigma'} \langle [B] \rangle = \frac{4}{3} \pi N (\sigma'^3 - \sigma^3) \left(\frac{d\phi}{dt} \right)_{\sigma'} \langle [B] \rangle + \frac{4}{3} \pi N (\sigma'^3 - \sigma^3) \cdot k(\phi)_{\sigma'} \langle [B] \rangle \quad (43)$$

The macroscopic bimolecular rate constant k_c (in $\text{mole}^{-1} \text{s}^{-1}$) is related to the rate constant k by the equation

$$\frac{\partial(C)}{\partial t} = k_c [A][B]_{\sigma'} = [A][B]_{\sigma'} N \int_{\sigma}^{\sigma'} 4\pi r^2 k dr$$

then

$$k_c = \frac{4}{3} \pi N (\sigma'^3 - \sigma^3) k = NV_1 k \quad (44)$$

By including this macroscopic term in Eq. (43), one obtains the following relation:

$$k_0 \sigma' \left(\frac{\partial \phi}{\partial r} \right)_{\sigma'} = NV_1 \left(\frac{d\phi}{dt} \right)_{\sigma'} + k_c (\phi)_{\sigma'} \quad (45)$$

where $k_0 = 4\pi N\sigma'D$.

Eqs. 42 and 45 together define the systems.

It is convenient to use the dimensionless terms $\rho = r/\sigma'$ and $\tau = Dt/\sigma'^2$; eqs. 42 and 45 become

$$\begin{aligned} \frac{\partial \phi}{\partial \tau} &= \frac{\partial^2 \phi}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial \phi}{\partial \rho} \\ \left(\frac{\partial \phi}{\partial \rho} \right)_1 &= \frac{1}{3} \left[1 - \left(\frac{\sigma}{\sigma'} \right)^3 \right] \left[\frac{\partial \phi}{\partial \tau} \right]_1 + \frac{k_c}{k_0} [\phi]_1 \end{aligned} \quad (46)$$

This system lends itself to resolution by Laplace transform techniques.

The transform $y(p)$ of $\phi(t)$, is defined as

$$y(p) = \int_0^{\infty} e^{-pt} \phi(t) dt$$

Then, we have (cf. Ref. 13)

$$[y(p)]_1 \equiv y_1(p) = \frac{1}{p} \left[1 - \frac{\beta}{\alpha p + \sqrt{p} + \beta + 1} \right]$$

with

$$\alpha = \frac{1}{3} \left[1 - \left(\frac{\sigma}{\sigma'} \right)^3 \right] \quad (47)$$

$$\beta = k_c/k_o$$

The value $\phi_1(\tau)$ of the distribution function at the distance $\sigma'(\rho = 1)$ gives several analytical solutions which depend on the value of the quantity $\alpha(\beta + 1)$.

(i) Case Where $\alpha(\beta + 1) = 0$

$$\phi_1(\tau) = \frac{1}{\beta + 1} + \frac{\beta}{\beta + 1} \exp [(\beta + 1)^2 \tau] \operatorname{Erfc} [(\beta + 1) \sqrt{\tau}] \quad (48)$$

This relation is similar to that proposed by Ware et al.,^{11,12} by Owen²¹ and Collins and Kimball.² However, this equation corresponds to the case where $\sigma' = \sigma$, whereas these authors assume $\sigma' > \sigma$, but do not take into account the accumulation of B corresponding to the term $NV_1(\partial\phi/\partial t)$.

(ii) Case Where $\alpha(\beta + 1) \in]0, 1/4[$

$$\phi_1(\tau) = \frac{1}{\beta + 1} - \frac{2\alpha\beta}{\gamma(1 + \gamma)} \exp \left[\left(\frac{1 + \gamma}{2\alpha} \right)^2 \tau \right] \operatorname{Erfc} \left[\left(\frac{1 + \gamma}{2\alpha} \right) \sqrt{\tau} \right]$$

$$+ \frac{2\alpha\beta}{\gamma(1 - \gamma)} \exp \left[\left(\frac{1 - \gamma}{2\alpha} \right)^2 \tau \right] \operatorname{Erfc} \left[\left(\frac{1 - \gamma}{2\alpha} \right) \sqrt{\tau} \right] \quad (49)$$

with $\gamma = \sqrt{1 - 4(\beta + 1)\alpha}$.

(iii) Case Where $\alpha(\beta + 1) = 1/4$

$$\phi_1(\tau) = (1 - 4\alpha^2) - 4\alpha^2 \left[\left(\frac{\tau}{2\alpha^2} - 1 \right) \exp \frac{\tau}{4\alpha^2} \operatorname{Erfc} \left(\frac{\sqrt{\tau}}{2\alpha} \right) - \frac{1}{\alpha} \sqrt{\tau/\pi} \right] \quad (50)$$

(iv) Case Where $\alpha(\beta + 1) > 1/4$

$$\begin{aligned} \phi_1(\tau) = & \frac{1}{\beta + 1} + \frac{2i\alpha\beta}{\gamma'} \left[\frac{1}{1 + i\gamma'} \exp \left[\left(\frac{1 - i\gamma'}{2\alpha} \right)^2 \tau \right] \operatorname{Erfc} \left[\left(\frac{1 - i\gamma'}{2\alpha} \right) \sqrt{\tau} \right] \right. \\ & \left. - \frac{1}{1 - i\gamma'} \exp \left[\left(\frac{1 + i\gamma'}{2\alpha} \right)^2 \tau \right] \operatorname{Erfc} \left[\left(\frac{1 + i\gamma'}{2\alpha} \right) \sqrt{\tau} \right] \right] \quad (51) \end{aligned}$$

with $i^2 = -1$, and $\gamma' = \sqrt{4\alpha(\beta + 1) - 1}$.

From above, one obtains

$$k_a(\tau) = NV_1 k \phi_1(\tau) = k_c \phi_1(\tau) \quad (52)$$

The variations of $k_a(\tau)$ are therefore given by the expression of $\phi_1(\tau)$.

At large values of time, the above relations can be simplified by using the Taylor series expansion of the transform $y_1(p)$. One obtains

$$\phi_1(\tau) \approx \frac{1}{\beta + 1} \left[1 + \frac{\beta}{\beta + 1} \frac{1}{\sqrt{\pi\tau}} \right] \quad (53)$$

and

$$k_a(t) \approx \frac{k_o k_c}{k_o + k_c} \left[1 + \frac{k_c}{k_c + k_o} \frac{\sigma'}{\sqrt{\pi Dt}} \right] \quad (54)$$

This simplified relation is identical to that proposed by Nemzek and Ware.¹²

The limit of $k_a(t)$ as t approaches infinity is

$$\lim_{t \rightarrow \infty} k_a = \frac{k_c}{1 + k_c/k_o}$$

or

$$\lim_{t \rightarrow \infty} \frac{1}{k_a} = \frac{1}{k_c} + \frac{1}{k_o} \quad (55)$$

and when k_c/k_o approaches infinity, $k_a(t)$ becomes

$$k_a(t) = k_o \left[1 + \frac{\sigma'}{\sqrt{\pi D t}} \right]$$

which is identical to Eq. (19), except for the value of $\bar{\sigma}$ which has been replaced by σ' .

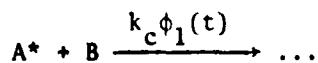
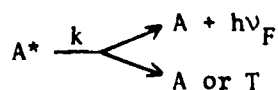
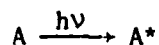
In the analysis of experiments on fluorescence quenching using conventional flash excitation, Eq. (54) can be used.¹³ If the phenomenon is recorded during a very short interval (several picoseconds), the former expression of $k_a(t)$ is no longer valid. A Taylor series of $y_1(p)$ in the term $1/\sqrt{p}$ leads to the following expression of $k_a(t)$ valid for short times

$$k_a(t) \approx k_c \left[1 - \frac{\beta}{\alpha} t + \frac{4}{3\sqrt{\pi}} \frac{\beta}{\alpha^2} t^{3/2} + \frac{\beta(\alpha\beta + \alpha - 1)}{2\alpha^3} t^2 - \frac{8\beta(2\alpha\beta + 2\alpha - 1)}{15\alpha^4\sqrt{\pi}} t^{5/2} + \dots \right] \quad (56)$$

Time evolution of the apparent rate constant k_a is given in Fig. 2 by using the three equations 51, 54 (for long times) and 56 (for short times). The range of validity for each equation is clear from the diagram.

6. CONSEQUENCES

Consider the following scheme for the deactivation of A^* :



After δ -pulse excitation,

$$\frac{d[A^*]}{dt} = - [(k + k_c[B]\phi_1(t))][A^*] \quad (57)$$

Transforming to non-dimensional variables as before,

$$\frac{1}{[A^*]} \frac{d[A^*]}{d} = - \left[\frac{k\sigma'^2}{D} + \frac{k_c\sigma'^2}{D} [B]\sigma_1(\tau) \right] \quad (58)$$

Then, if we define

$$Z(\tau) \equiv \log \frac{[A^*]}{[A^*]_{\tau=0}}$$

and

$$A_1 = \frac{k\sigma'^2}{D}$$

$$A_2 = \frac{k_a\sigma'^2}{D} [B]$$

we obtain

$$\frac{dZ}{d\tau} = -A_1 - A_2\phi_1(\tau) \quad (59)$$

It is possible to resolve this system using Laplace transforms. One obtains

$$pZ(p) - Z(0) = \frac{A_1}{p} - A_2\gamma_1(p)$$

with

$$\gamma_1(p) = \int_0^{\infty} e^{-pt} \phi_1(t) dt$$

leading in Laplace transform space to

$$Z(p) = \frac{A_1}{p^2} - \frac{A_2}{p^2} + \frac{A_2\beta}{p^2} \frac{1}{\alpha p + \sqrt{p} + \beta + 1} \quad (60)$$

It is also possible to obtain the value $Z(\tau)$, of the decay function of A^* . Several analytical solutions are obtained which depend on the value of the product $\alpha(\beta + 1)$ (cf. Ref. 13):

(i) Case Where $\alpha(\beta + 1) = 0$

$$Z(\tau) = - \left(A_1 + \frac{A_2}{\beta + 1} \right) \tau - \frac{2A_2\beta}{(\beta + 1)^2} \sqrt{\tau/\pi} + \frac{A_2\beta}{(\beta + 1)^3} [1 - \exp((\beta + 1)^2 \tau) \operatorname{Erfc}((\beta + 1)\sqrt{\tau})] \quad (61)$$

(ii) Case Where $\alpha(\beta + 1) \in]0, 1/4[$

$$Z(\tau) = - \left(A_1 + \frac{A_2}{\beta + 1} \right) \tau - \frac{2A_2\beta}{(\beta + 1)^2} \sqrt{\tau/\pi} + \frac{A_2\beta(1 - \alpha(\beta + 1))}{(\beta + 1)^3} + \frac{8\pi^3 A_2\beta}{\gamma} \left[\frac{1}{(1 + \gamma)^3} \exp\left(\frac{4\alpha^2 \tau}{(1 + \gamma)^2}\right) \operatorname{Erfc}\left[\left(\frac{2\alpha}{1 + \gamma}\right)\sqrt{\tau}\right] - \frac{1}{(1 - \gamma)^3} \exp\left(\frac{4\alpha^2 \tau}{(1 - \gamma)^2}\right) \operatorname{Erfc}\left[\left(\frac{2\alpha}{1 - \gamma}\right)\sqrt{\tau}\right] \right] \quad (62)$$

with $\gamma = \sqrt{1 - 4\alpha(\beta + 1)}$

(iii) Case Where $\alpha(\beta + 1) = 1/4$

$$Z(\tau) = - \left(A_1 + \frac{A_2}{\beta + 1} \right) \tau - \frac{2A_2\beta}{(\beta + 1)^2} \sqrt{\tau/\pi} + \frac{3A_2\beta}{4(\beta + 1)^3} + \frac{A_2\beta}{4(\beta + 1)^3} \left[\left(2(\beta + 1)^2 \tau - \frac{3}{4} \right) \operatorname{Erfc}\left(\frac{\sqrt{\tau}}{2\alpha}\right) \cdot \exp\left(\frac{\tau}{4\alpha^2}\right) \right] \quad (63)$$

(iv) Case Where $\alpha(\beta + 1) > 1/4$

$$Z(\tau) = - \left(A_1 + \frac{A_2}{\beta + 1} \right) \tau - \frac{2A_2\beta}{(\beta + 1)^2} \sqrt{\tau/\pi} + \frac{A_2\beta(1 - \alpha(\beta + 1))}{(\beta + 1)^3} + \frac{8\alpha^3 A_2\beta}{\gamma'} i \left[\frac{i}{(1 - i\gamma')^3} \exp\left[\frac{4\alpha^2}{(1 - i\gamma')^2} \tau\right] \operatorname{Erfc}\left[\frac{2\alpha}{(1 - i\gamma')} \sqrt{\tau}\right] \right]$$

$$- \frac{1}{(1 + i\gamma')^3} \exp\left[\frac{4\alpha^2}{(1 + i\gamma')^2} \tau\right] \operatorname{Erfc}\left[\frac{2\alpha}{(1 + i\gamma')} \sqrt{\tau}\right] \quad (64)$$

with $i^2 = -1$ and $\gamma' = \sqrt{4\alpha(\beta + 1) - 1}$

These different expressions lead to variations of the value

$$y = \left[Z(\tau) + \left(A_1 + \frac{A_2}{\beta + 1} \right) \tau + \frac{2A_2\beta}{(\beta + 1)^2} \sqrt{\tau/\pi} \right] / A_2$$

as it is shown in Fig. 3.

As can be seen from Fig. 3, for values of τ of the order of magnitude of unity, or greater than unity, the difference between $Z(\tau)$ and the decay function $Z'(\tau)$, which contains only terms proportional to τ and $\sqrt{\tau}$, i.e.,

$$Z'(\tau) = - \left(A_1 + \frac{A_2}{\beta + 1} \right) \tau - \frac{2A_2\beta}{(\beta + 1)^2} \sqrt{\tau/\pi}$$

is practically constant.

The expression of $Z'(\tau)$ can be obtained (Eq. (54)) from the simplified expression of $\phi_1(\tau)$, then $\phi_1'(\tau)$. The curves presented in Fig. 3 show only the difference between Z and Z' divided by A_2 .

(i) $Z(\tau) < Z'(\tau)$ for $\alpha(\beta + 1) > 1$ when $\phi_1'(\tau)$ is always greater than $\phi_1(\tau)$. This occurs particularly in the case presented in paper I;¹ the expression for $Z(\tau)$ in this important case, when the reaction is practically limited by diffusion, is given by

$$Z(t) = -NV_1[B] - [(k + k_0[B])t + 2k_0B\sigma' \sqrt{(t/\pi D)}]$$

(ii) $Z(\tau) > Z'(\tau)$ for $\alpha(\beta + 1) < 1$. This result is obtained for the conditions where $\phi_1'(\tau)$ can be less than $\phi_1(\tau)$. The results can be understood with the aid of the qualitative curves in Fig. 4 and from the Taylor series of $Z(\tau)$ obtained for large values of τ .

$$\begin{aligned} Z(\tau) = & - \left(A_1 + \frac{A_2}{\beta + 1} \right) \tau - \frac{2A_2\beta}{(\beta + 1)^2} \sqrt{\tau/\pi} - \frac{A_2\beta}{(\beta + 1)^3} [\alpha(\beta + 1) - 1] \\ & + \frac{A_2\beta[2\alpha(\beta + 1) - 1]}{(\beta + 1)^4} \frac{1}{\sqrt{\pi\tau}} + \dots \end{aligned} \quad (65)$$

As can be seen in Fig. 3, for small values of τ (≥ 0.2), termination of the expression (65) after the constant term yields a good approximation of the time evolution of $Z(\tau)$. By replacing A_1 and A_2 , we obtain

$$Z(t) \approx - \left[k + \frac{k_c k_o}{k_c + k_o} [B] \right] t - \frac{k_c^2 k_o}{(k_c + k_o)^2} [B] \frac{2\sigma'}{\sqrt{\pi D t}} - NV_1' [B] \quad (66)$$

i.e.,

$$Z(t) = -at - b\sqrt{t} - c$$

with

$$NV_1' = 4\pi N\sigma' \frac{k_c^2 k_o}{(k_c + k_o)^3} \left[\alpha \left(1 + \frac{k_c}{k_o} \right) - 1 \right]$$

Using the approximate form of the above equations, it is then possible to analyze data from the following experiments:

(i) Single Photon Counting. One can obtain the values

$$\frac{k_o k_c}{k_c + k_o} \text{ and } \frac{k_c}{k_c + k_o} \frac{\sigma'}{\sqrt{D}}$$

Also, the variation of k_c/k_o can be studied by measuring the effect of viscosity to the reaction between A^* and B. Then, knowing k_o , k_c can be calculated. It is thus possible to calculate all the essential kinetic parameters of the reaction.

(ii) Steady-State Fluorescence Measurements. When the lifetime of A^* , in the absence of B, is short (less than 10 ns) it is not possible to find a good decay function of the form $\exp(-at - b\sqrt{t} - c)$ in which a, b and c are constants. For these conditions, only steady-state fluorescence measurements lead to the determination of the kinetics parameters for the reactions between A^* and B.

When A^* is a singlet excited state, we can measure the quantum yield of fluorescence of A^* in the presence (I) or in the absence (I_o) of B, all other experimental conditions being constant.

Then, all other conditions being constant, for the steady-state experiment, the ratio of I_o over I can be expressed as done above by

$$\frac{I_o}{I} = \frac{\int_0^{\infty} (A^*)_{[B]=0} dt}{\int_0^{\infty} (A^*)_{[B] \neq 0} dt}$$

$$\frac{I_o}{I} \approx \frac{1}{k} \frac{1}{e^{-NV_1'[B]} \int_0^{\infty} \exp \left(- \left[k + \frac{k_o k_c}{k_o + k_c} [B] \left(1 + \frac{k_c}{k_o k_c} \frac{2\sigma'}{\sqrt{\pi D \tau}} t \right) \right] \right) dt}$$

leading to

$$\frac{I_o}{I} \approx \frac{e^{NV_1'[B]}}{I(\lambda')} \left[1 + \frac{k_o k_c}{k_o + k_c} \tau_o [B] \right] \quad (67)$$

with $\tau_o = 1/k$; with $I(\lambda') = \int_0^{\infty} \exp(-a - \lambda' \sqrt{u}) du$ (1) and

$$\lambda' = \frac{2\sigma'}{\sqrt{\pi D \tau}} \frac{k_c^2 k_o \tau_o [B]}{(k_c + k_o)^2} \frac{1}{\sqrt{1 + \frac{k_c k_o}{k_c + k_o} \tau_o [B]}}$$

For small quencher concentrations, the first and the second terms of the Taylor series of ϕ_o/ϕ versus B are:

$$\frac{I_o}{I} = 1 + \left\{ NV_1' + \frac{k_o k_c}{k_o + k_c} \tau_o \left(1 + \frac{k_c}{k_o + k_c} \frac{\sigma'}{\sqrt{D \tau_o}} \right) \right\} [B] + \dots$$

All other terms in this expression can be neglected. Then, the apparent constant of quenching K_{SV} is equal to:

$$K_{SV} = NV_1' + \frac{k_o k_c}{k_o + k_c} \tau_o \left[1 + \frac{k_c}{k_o + k_c} \frac{\sigma'}{\sqrt{D \tau_o}} \right] \quad (68)$$

For short times (smaller than about 1 ns), a Taylor series of

$Z(p)$ lead to the following expression of $Z(\tau)$:

$$Z(\tau) = - (A_1 + A_2)\tau + \frac{A_2\beta}{\alpha} \frac{\tau^2}{2} - \frac{A_2\beta}{\alpha^2} \frac{8}{15\sqrt{\pi}} \tau^{5/2} + \frac{A_2\beta}{\alpha^3} (1 - \alpha(\beta + 1)) \frac{\tau^3}{6} + \dots \quad (69)$$

7. EXPERIMENTAL RESULTS

In their study of the quenching of 1,2-benzanthracene by CBr_4 , Ware and Nemzek¹² verified that the decay law for this system when propane diol was used as solvent was not a single exponential, but could be adequately fit by $\exp\{-at - bt^{1/2}\}$. This is illustrated in Fig. 4. From Eqs. (26) and (27), the σ values were obtained along with the values of D . These are listed in Table 1. If these values are used in Eq. (29), they fail to reproduce the steady state behaviour by a wide margin (see dashed line, Fig. 5). On the other hand, the diffusion coefficients are reasonable.

This discrepancy is resolved by using Eq. (38) and seeking the best values of σ' and D consistent with the set of data represented by the points in Fig. 5. σ was determined by Lebas' theory.²² The values of σ' and D are in excellent agreement with those obtained from $\exp\{-at - bt^{1/2}\}$. This is illustrated by the solid lines in Fig. 5 which were calculated from $\sigma' = 8.8 \text{ \AA}$ and the values of D .

The decay law $\exp\{-at - bt^{1/2}\}$ has also been verified for the quenching of pyrene by biacetyl.²³ From Eq. (66), the values of a and b yield $[k_c/(k_o + k_c)]\sigma'$ and D . This approach, when used on decay data analyzed either by iterative reconvolution or deconvolution via the fast Fourier transform technique,²⁴ yielded values of $[k_c/(k_c + k_o)]\sigma'$ of 9.1 \AA and $D = 1.53 \times 10^{-6} \text{ cm}^2/\text{sec}$ for the quenching of pyrene by biacetyl in 75% cyclohexane - 25% cyclohexane solvent at 22°C (viscosity = 42 cp). The fit is illustrated in Figs. 6 and 7. Eq. (66) requires the terms a and b to depend on concentration. This is illustrated in Fig. 8. From the variation of the quenching with viscosity, k_c is estimated to be about $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. At high viscosity where the value of $[k_c/(k_c + k_o)]\sigma'$ was determined to be 9.1 \AA , $k_c \gg k_o$ and thus $\sigma' = 9.1 \text{ \AA}$. From the molecular dimensions,²² one calculates $\sigma = 6.5 \text{ \AA}$ in keeping with the general pattern observed in diffusion controlled processes.

A further example, where the formalism presented above has been employed, is the system of POPOP quenched by CBr_4 in mixed cyclohexanol-cyclohexane solvents.²³ As can be seen from Fig. 9, strongly non-linear Stern-Volmer plots are obtained. Analysis using Eq. (68)

yielded the $[k_c/(k_c + k_o)]\sigma' \approx 9 \text{ \AA}$ over a range of viscosity of 1.3 to 24 cp. From the analysis of the variation of $[(k_o + k_c)/k_c]\sigma'$ as a function of diffusion coefficient, k_c is estimated to be $3 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. For the viscosity range of the experiment of Ware and Nemzek¹²

$$0.98 \leq k_c/(k_c + k_o) < 0.998$$

Thus, POPOP quenched by CBr_4 in propane diol should be essentially diffusion controlled.

This lends support to the assumption of Ware and Nemzek¹² that the quenching of 1,2-benzanthracene by CBr_4 is controlled in propane diol.

Application of the above formalism to fluorescence polarization studies of quenching have also been made by Andre, Bouchy and Ware.²³

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TABLE 1. Values of σ' and D which give the best fits to decay curves (from Nemzek and Ware)¹² and to steady-state experiment of 1,2-benzanthracene quenched by CBr_4 in propane-diol.

CBr_4 Concentration (M)	σ' (Å)			D $10^6 \text{ cm}^2 \text{ s}^{-1}$		
	15°C	25°C	35°C	15°C	25°C	35°C
from decay curves						
0.098	9.0	8.5	8.5	0.23	0.50	0.88
0.18	9.0	9.0	8.0	0.24	0.44	0.95
0.29	8.0	7.0	7.0	0.28	0.66	1.1
steady-state experiments (classical model) (Ref. 12)						
	11.2	-	-	0.287	-	-
steady-state experiments (Ref. 23)						
	8.8	8.8	8.8	0.37	0.59	1.01

Figure 1. Separation of space into two volumes where chemical reaction ($r < \sigma'$) and diffusion ($r > \sigma'$) occur. (A) Distribution at $t = 0$. (B) Distribution at $t > 0$.

Figure 2. Substitution of the true value of $\phi_1(\tau)$ by Taylor series ($\alpha = 0.3$ and $\beta = 0.5$): (1) True analytical function of $\phi_1(\tau)$; (2) Taylor series for short values of τ (Eq. 56); (3) Taylor series for large values of τ (Eq. 54).

Figure 3. Variation of $Y = \{Z(\tau) + [A_1 + A_2/(\beta + 1)]\tau + 2A_2\beta/(\beta + 1)^2 (\tau/\pi)^{1/2}\}/A_2$ versus τ (see text). $\beta = 5$. (1) $\alpha = 0$; (2) $\alpha = 1/6$; (3) $\alpha = 2/3$; (4) $\alpha = 1/3$.

Figure 4. Open points: flashlamp. Solid points: observed fluorescence decay of 1,2-benzanthracene in 1,2-propanediol quenched by 0.29 M CBr₄. At 30° C. Dashed line: attempt to fit with $G(t) \propto \exp\{t/\tau\}$ to minimize the sum of the squares of the weighted residuals. Solid line: fit with $G(t) = \exp(-at - 2b\sqrt{t})$ by iterative convolution. Best a and b give $R' = 7.5 \text{ \AA}$ and $D_{AQ} = 0.79 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$.

Figure 5. Steady-state experiments of fluorescence quenching of 1,2-benzanthracene by CBr₄ in 1,2-propanediol at different temperatures: (A) 15° C; (B) 25° C; (C) 35° C. Solid lines: calculated from Eq. (10) with parameters from Table 1 (our model). Dashed line: calculated from Eq. (20) for 15° C.

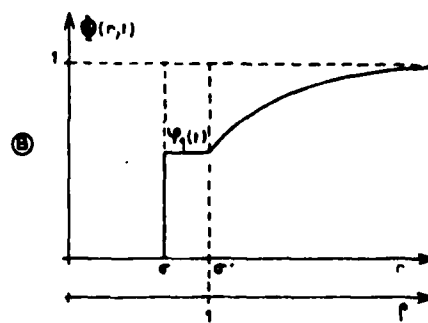
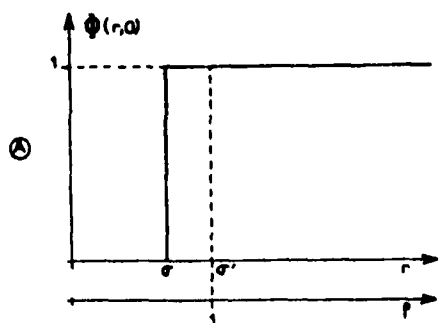
Figure 6. (1) Flash lamp, (2) observed fluorescence decay of pyrene in mixing 75% cyclohexanol, 25% cyclohexane as solvent at 22° C, quenched by biacetyl (0.0677 mole ℓ^{-1}). (a) Attempt to fit with $G(t) \propto \exp(-t/\tau)$ to minimize the sum of the squares of the weighted residuals. (b) Fit with $G(t) = \exp(-at - bt^2)$ by iterative convolution ($a = 6.3 \times 10^7 \text{ M}^{-1}$, $b = 7.1 \times 10^5 \text{ ns}^{-2}$). ℓ channel = 0.44 ns.

Figure 7. (a) Deconvoluted curve of fluorescence decay of pyrene, in mixing 75% cyclohexanol, 25% cyclohexane as solvent, at 22° C, quenched by biacetyl (0.0677 mol ℓ^{-1}) by using Fast Fourier transform programme. (b) (1) Flash lamp; (2) observed fluorescence decay of pyrene; (3) flash lamp convoluted with the curve a. ℓ channel = 0.285 ns.

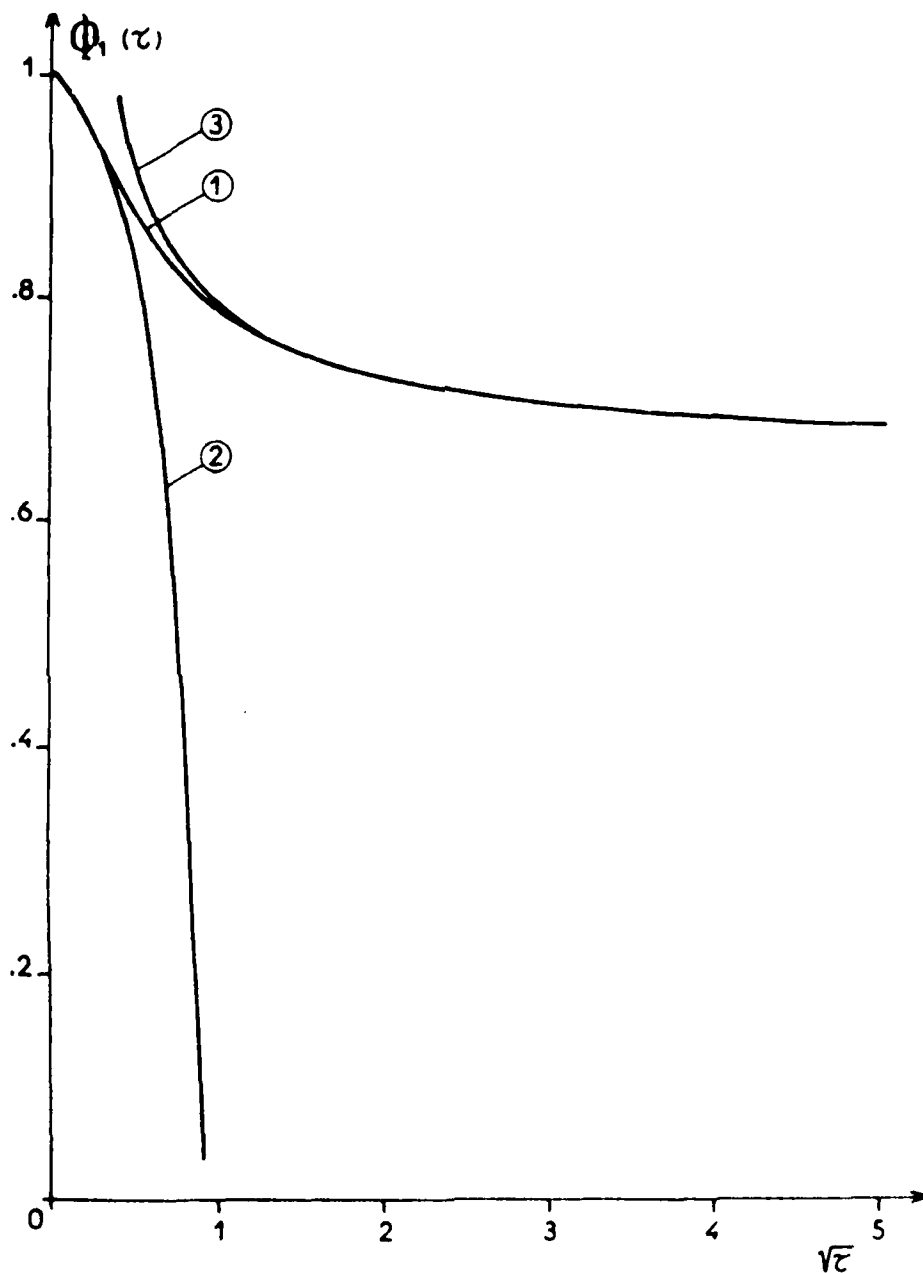
Figure 8. Variations of (a) and (b) with (biacetyl).

Figure 9. Steady-state fluorescence experiments: variation of ϕ_0/ϕ versus (CBr₄). (1) $\eta = 1.32 \text{ cp}$; (2) $\eta = 2.04 \text{ cp}$; (3) $\eta = 2.47 \text{ cp}$; (4) $\eta = 3.02 \text{ cp}$; (5) $\eta = 6.72 \text{ cp}$; (6) $\eta = 11.63 \text{ cp}$; (7) $\eta = 24 \text{ cp}$, $\theta = 22^\circ \text{ C}$.

THE INFLUENCE OF DIFFUSION ON FLUORESCENCE QUENCHING



THE INFLUENCE OF DIFFUSION ON FLUORESCENCE QUENCHING



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THE INFLUENCE OF DIFFUSION ON FLUORESCENCE QUENCHING

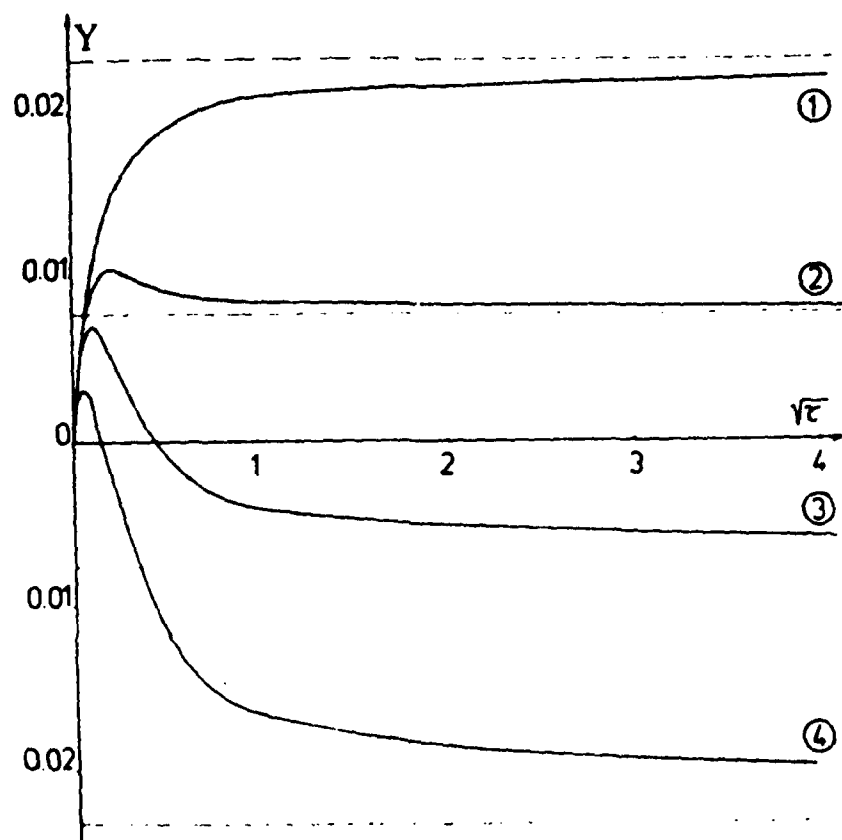
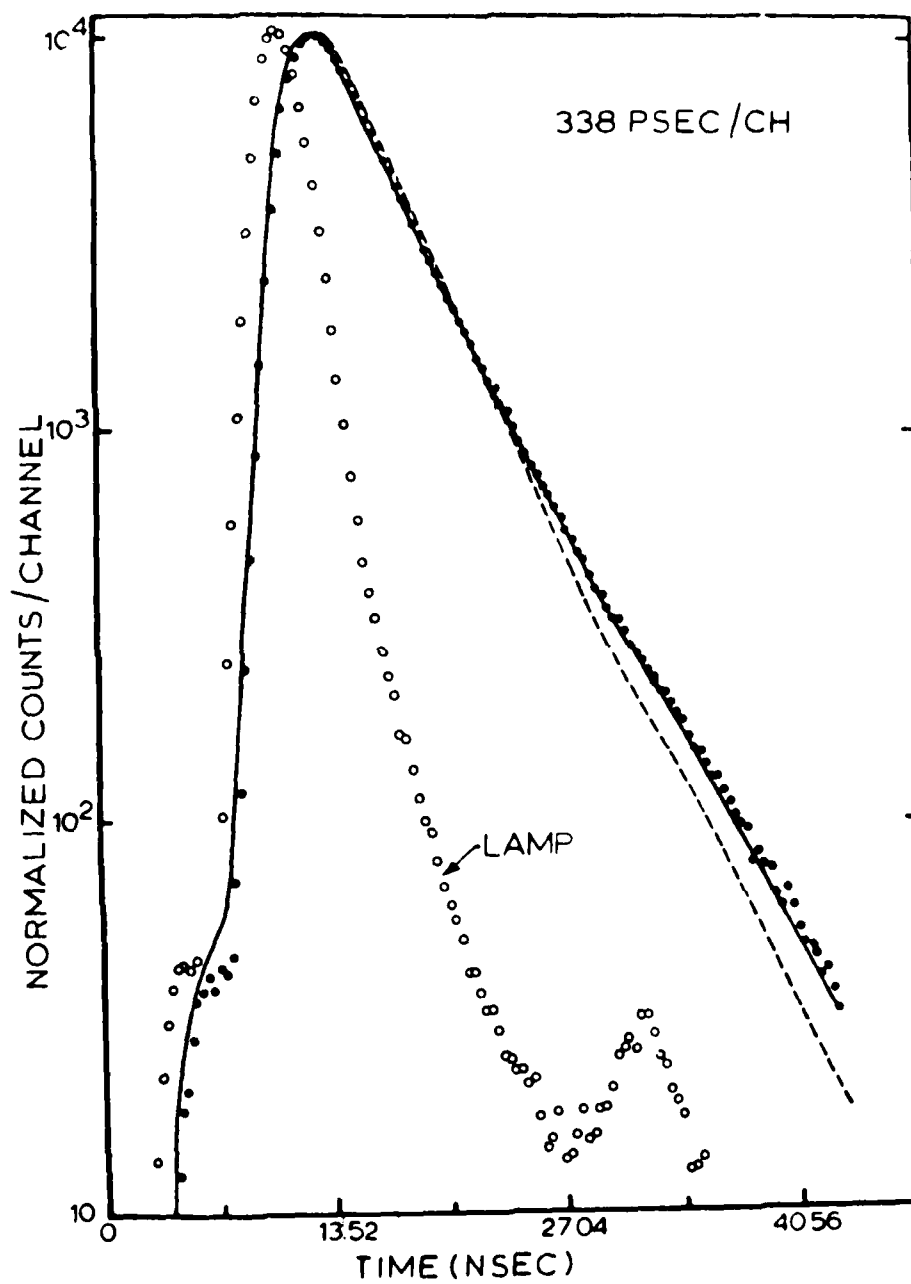


Fig 3

THE INFLUENCE OF DIFFUSION ON FLUORESCENCE QUENCHING



16.4

THE INFLUENCE OF DIFFUSION ON FLUORESCENCE QUENCHING

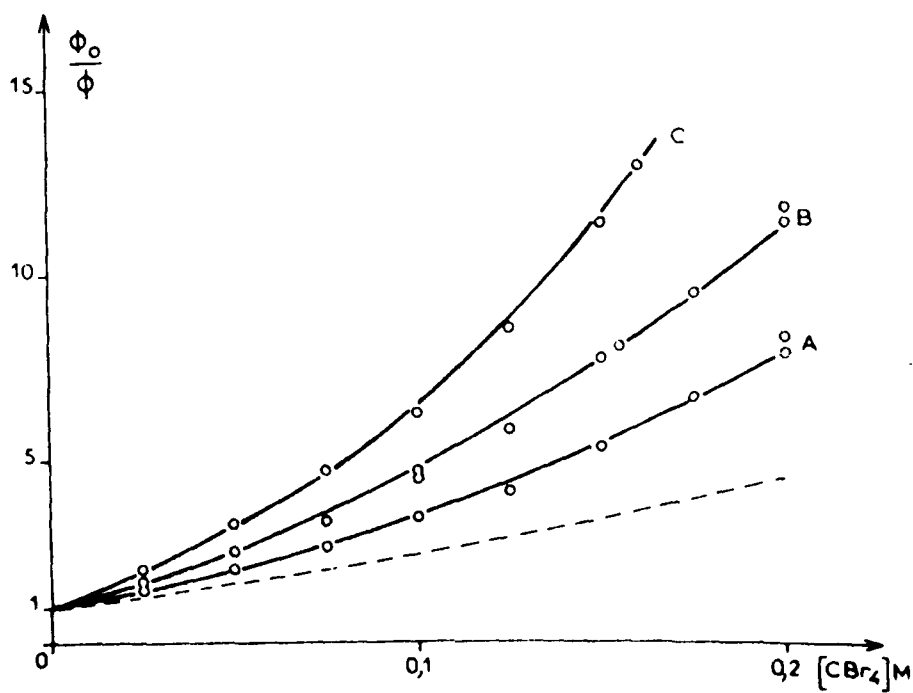


FIG. 5

THE INFLUENCE OF DIFFUSION ON FLUORESCENCE QUENCHING

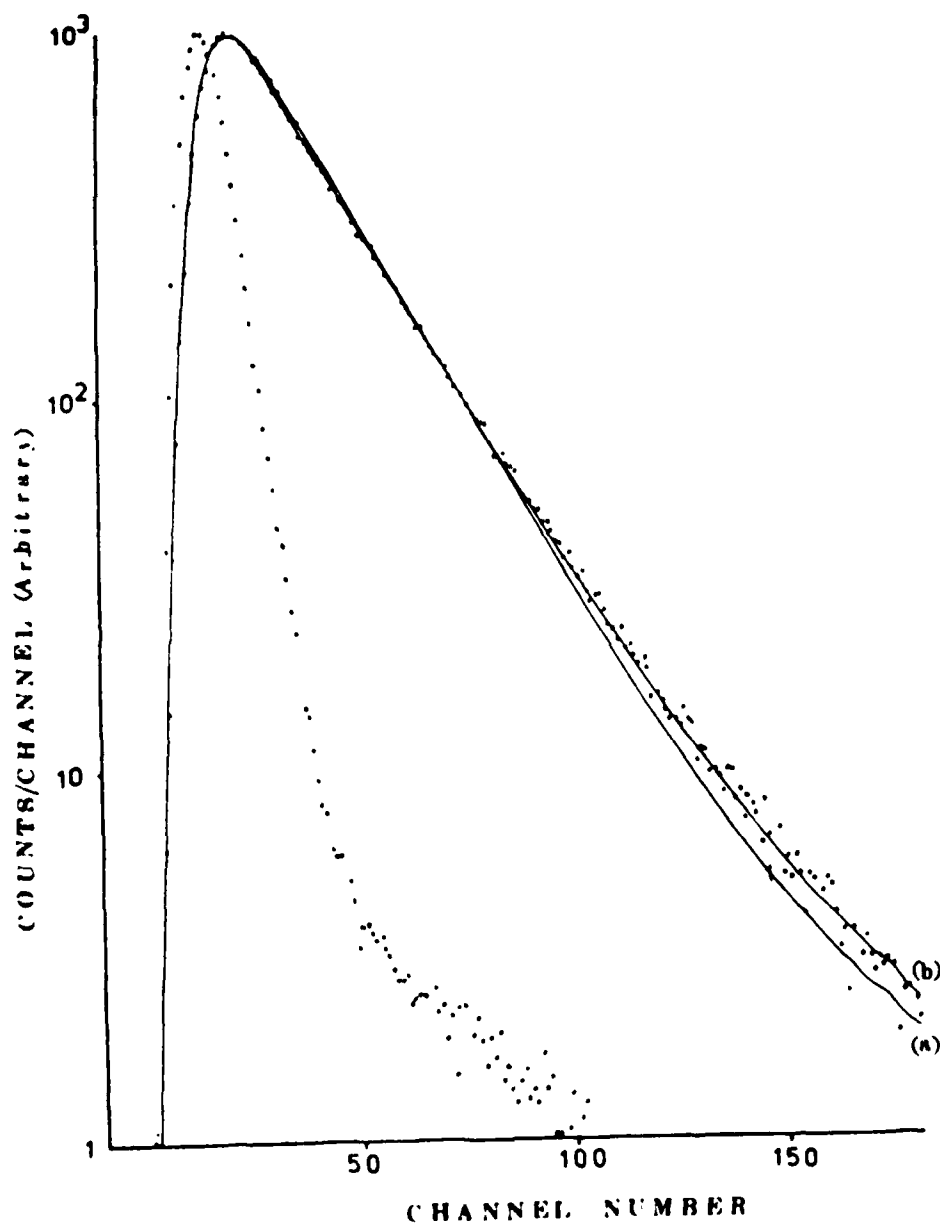


Fig. 6

THE INFLUENCE OF DIFFUSION ON FLUORESCENCE QUENCHING

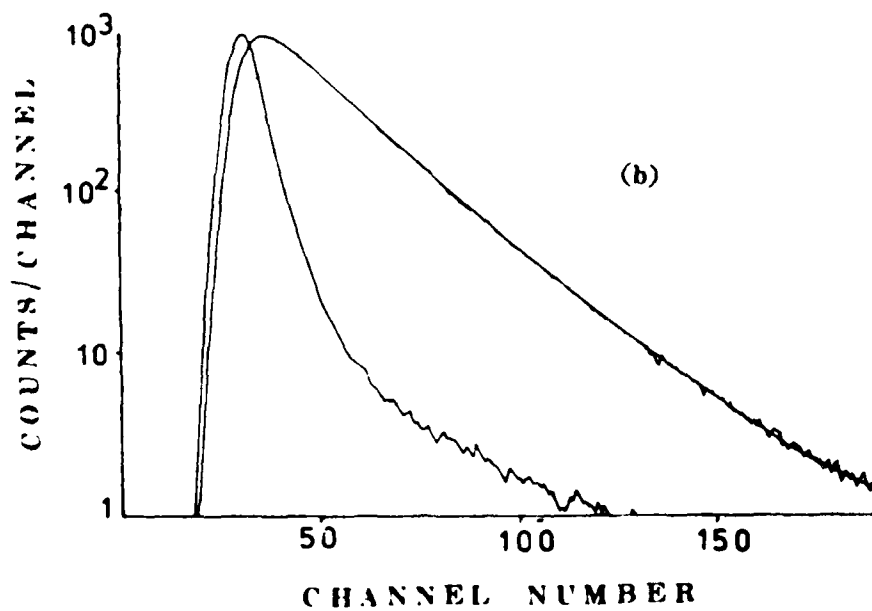
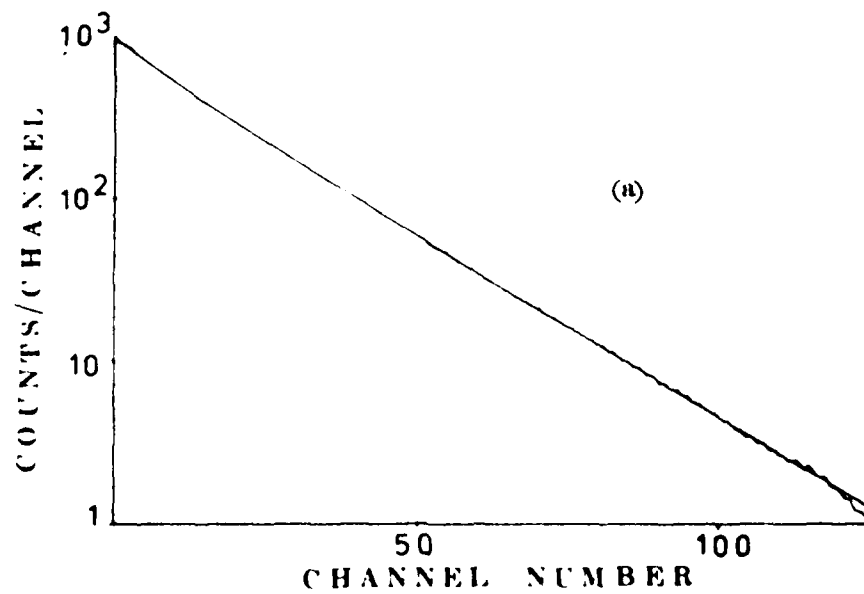


Fig 7

THE INFLUENCE OF DIFFUSION ON FLUORESCENCE QUENCHING

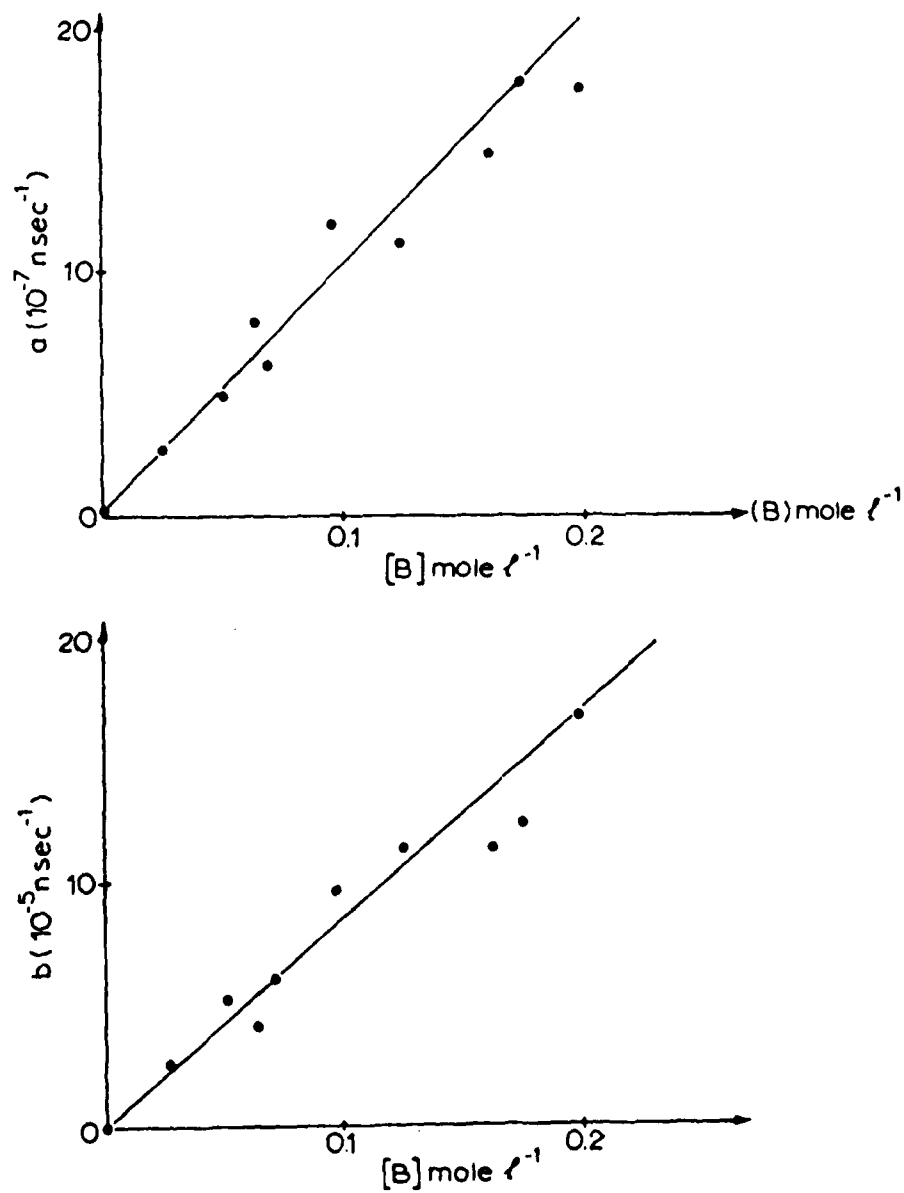


FIG. 8

THE INFLUENCE OF DIFFUSION ON FLUORESCENCE QUENCHING

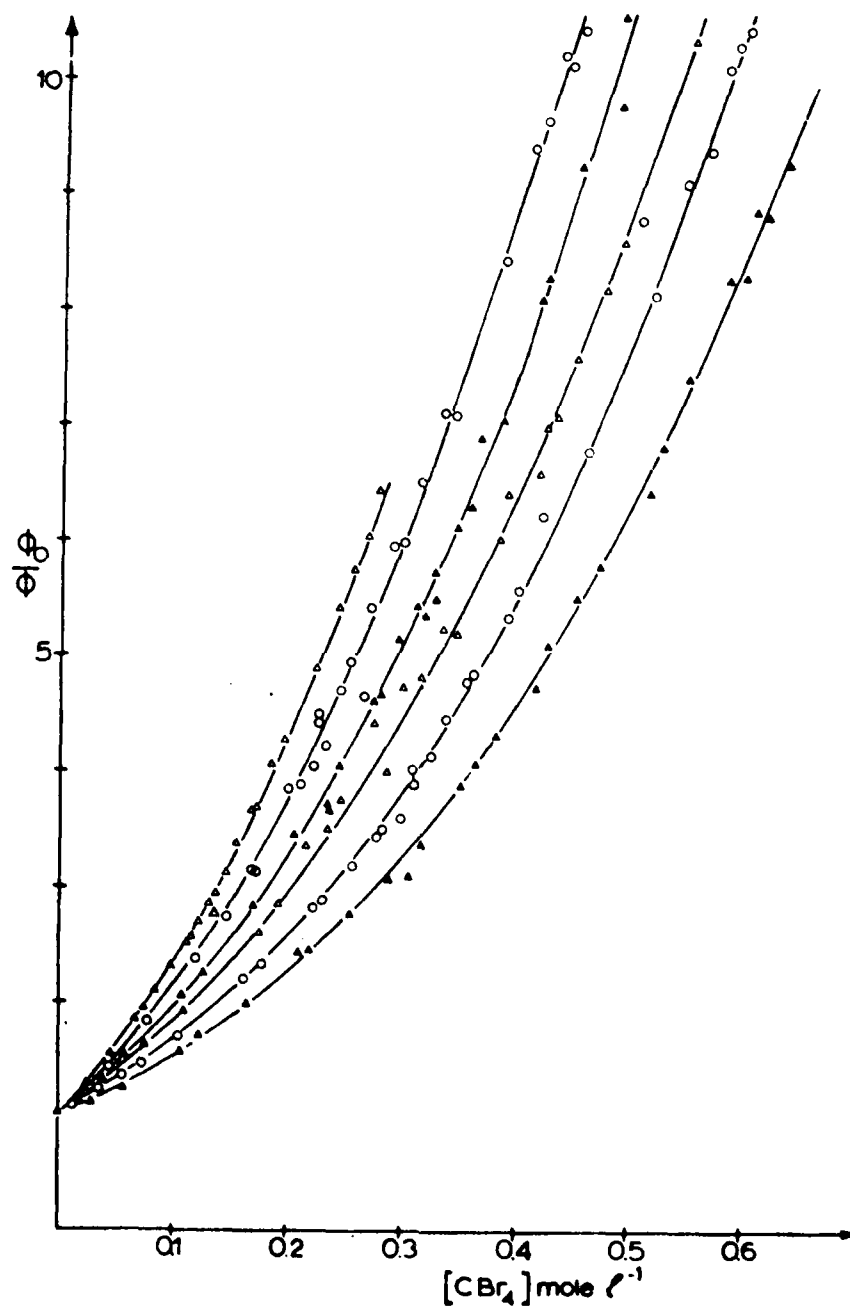


Fig 9

SECTION II

EXCIPLEX PHOTOPHYSICS

While exciplexes have been known for several decades, there has been remarkably little work reported in which the details of the kinetics are examined with sufficient precision and over a sufficient range of condition such that a critical test of proposed kinetic models is possible. Even the simple "Excimer" model for the kinetics involves a minimum of six rate constants. In what follows the recent work along these lines done to elucidate the details of exciplex photokinetics is reports.

The photophysics of systems exhibiting molecular association both in the ground and excited states has been studied. The emphasis has been on kinetic models, the measurement of rate constants associated with these models, and the determination of activation parameters and equilibrium thermodynamic parameters associated with the exciplex formation and disappearance. Studies of solvent effects and steric effects on the behaviour of exciplex systems have been carried out. The case of rapid equilibrium where the monomer and exciplex decay with the same rate constant has also been examined.

1. INTRODUCTION

The terms "excimer" and "exciplex" are used to describe molecular or atomic aggregates which are unstable in their ground states but possess significant binding energy in their electronically excited states. The term excimer was first used by Stevens and Hutton¹ to describe aggregates of like molecules. The term exciplex is due to Walker, Bender and Lumry² and pertains to the association of unlike species. Mataga, Okada and Ochari³ introduced the descriptive term "heteroexcimer" for the exciplex and both are in common use today. However, the phenomena described by these terms predates the nomenclature. Förster and Kasper⁴ first observed the characteristic red-shifted exciplex emission in concentrated pyrene solutions and Leon-

hardt and Weller⁵ were the first to observe exciplex emission in the system perylene quenched by N,N-dimethylaniline.

Excited states of EDA (electron donor-acceptor) complexes formed by direct excitation into the CT band have many properties in common with exciplexes and in general differ only in the ground state stability.^{6,7}

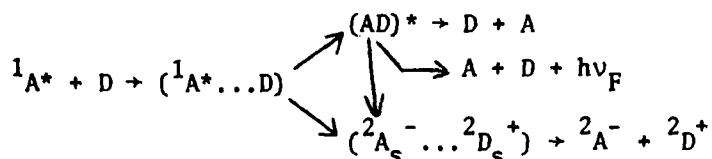
Excimers and exciplexes play an important role in photochemical transformations.⁸ In the exciplex, one has exchange and charge transfer interactions which hold the pair in close proximity allowing for the possibility of dimerization. In the exciplex, one has not only a large charge separation in the bound excited complex, but radical ions can be generated in the exciplex dissociation process in polar media. In addition, triplet formation via the exciplex is well established. Thus, in polar solvents, one frequently sees radical ion chemistry from exciplex forming systems with the "photochemistry" acting merely to generate radicals. Excited charge-transfer complexes can also serve as intermediates in photochemical reactions.⁹

2. PRIMARY PROCESSES IN EXCIPLEX SYSTEMS

Two aspects related to the primary processes in exciplex systems have generated considerable controversy over the past 15 years. One concerns the question of radical ion generation directly from the encounter complex prior to relaxation to form the bound exciplex. The other question concerns the formation of triplet states through the donor-acceptor interaction, but without the bound exciplex acting as an intermediate (the so-called "fast" triplet production).

The first problem had its origin in the observation^{10,11} that the exciplex emission yield fell off much more rapidly than the exciplex lifetime as the solvent dielectric constant was raised from 2.5 to 10. Mataga and co-workers initially attributed this to a decline in the exciplex radiative lifetime as well as to enhanced radiationless processes as the solvent polarity increased.¹²

Weller and co-workers¹³ argued that as the polarity of the solvent increased, the direct generation of radical ions took place from the encounter complex. These ideas can be combined in the following scheme:

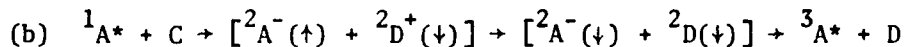


where $({}^2A_s^- \dots {}^2D_s^+)$ is the solvent shared ion pair. Laser photocon-

ductivity studies of Mataga and co-workers¹⁴ provide evidence for the direct generation of the solvent shared ion pair from the encounter complex. However, they also observed the growth of conductivity matching the decay of the exciplex thus confirming the path whereby the exciplex thermally dissociates into radical ions. There is also direct evidence for the sensitivity of the rate of exciplex emission to solvent polarity,¹⁵ but the effects are not large. Thus, the scheme presented above is probably correct in general, but with solvent effects present in most if not all of the individual steps.

In non-polar solvents, the energy of dissociation of the exciplex is high and the exciplex does not dissociate into radical ions to a significant extent. This simplifies the photophysics somewhat.

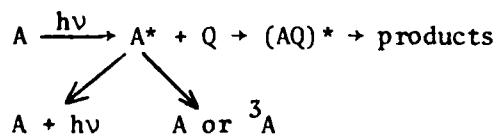
The second controversial topic relates to triplet production and can be illustrated by two quite different schemes:



In non-polar solvents, it appears that process (a) is the only important one and that process (b), which would generate the triplet via a fast process which bypasses the exciplex, does not occur to a significant extent.¹⁶ However, in highly polar solvents, the weight of the evidence points toward process (b) and the existence of a "fast" triplet generation route. The currently popular model involves hyperfine coupling interactions in the radical ion pair in highly polar solvents.^{16,17}

3. KINETIC ASPECTS OF EXCIMER AND EXCIPLEX PHOTOPHYSICS

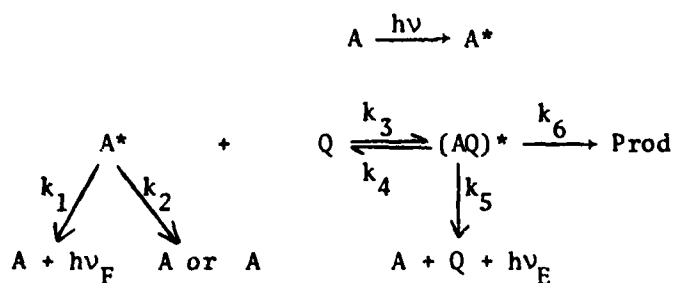
The simplest reaction scheme for quenching is



In this scheme, there is no regeneration of A^* from $(AQ)^*$ and the photokinetics correspond to ordinary fluorescence quenching kinetics. $(AQ)^*$, being non-emissive in this scheme, remains an elusive transient species, detectable perhaps by absorption spectroscopy. Its presence as an intermediate may be inferred from the products observed (e.g., products of radical ion reactions), but frequently, one can only guess as to the structure and properties of this intermediate. The rate of the forward or quenching reaction will probably be diffusion controlled which limits the information available from

photophysical studies. Nevertheless, the transient may be a genuine exciplex which is merely very unstable relative to products in the solvent used.

The next level of complexity introduces reversibility and exciplex fluorescence ($h\nu_E$).



Whether or not exciplex emission is measurable depends on equipment sensitivity, the ratio $k_5/(k_4 + k_5 + k_6)$, and the ratio

$$k_3[Q]/(k_1 + k_2 + k_3).$$

These photokinetics require that

$$[A^*](t) = a_1 e^{-\lambda_1 t} + a_2 e^{-\lambda_2 t} \quad (1)$$

$$[(AQ)^*](t) = a_3 (e^{-\lambda_1 t} + e^{-\lambda_2 t}) \quad (2)$$

where

$$\begin{aligned}
 \lambda_{1,2} = 1/2 [k_1 + k_2 + k_3[Q] + k_4 + k_p \pm \{(k_1 + k_2 + \\
 + k_3[Q] - k_4 - k_p)^2 + 4k_3k_4[Q]\}^{1/2}]
 \end{aligned} \quad (3)$$

and

$$k_p = k_5 + k_6 \quad (4)$$

Steady-state analysis gives (where ϕ_M and ϕ_E represent the quantum yields of monomer and exciplex, respectively)

$$\left(\frac{\phi_M^0}{\phi_M} - 1 \right) = \frac{k_3 k_p [Q]}{(k_4 + k_p)(k_1 + k_2)} \quad (5)$$

and

$$\frac{\phi_E}{\phi_M} = \left(\frac{k_5}{k_1} \right) \frac{k_3[Q]}{(k_4 + k_p)} \quad (6)$$

In the above equations, it has been assumed that $k_3 \neq f(t)$. Rate constants can then be determined as follows:

- k_1 : from the unquenched lifetime $(\tau)_{Q=0} = (k_1 + k_2)^{-1}$ and the quantum yield $\phi_M^0 = k_1/(k_1 + k_2)$.
- k_2 : from k_1 and $(\tau)_{Q=0}$.
- k_3 : from the slope of $(\lambda_1 + \lambda_2)$ vs. $[Q]$, since $\lambda_1 + \lambda_2 = (k_1 + k_2 + k_3[Q] + k_4 + k_p)$.
- k_4 and k_p : from a plot of $\lambda_1\lambda_2$ vs $[Q]$ since $\lambda_1\lambda_2 = (k_1 + k_2)(k_4 + k_p) + k_p k_3[Q]$. One obtains $k_4 + k_p$ from the intercept and k_p from the slope. Since k_3 is known, k_4 is calculated from $k_4 + k_p$. Problems obviously arise here if $k_4 \ll k_p$.
- k_5 : from Eq. (6), k_5 is obtained by plotting ϕ_E/ϕ_M vs $[Q]$. The slope gives

$$\frac{k_5}{k_1} \frac{k_3}{k_4 + k_p}$$

from which k_5 is calculated since all other rate constants are known.

- k_6 : since $k_p = k_5 + k_6$, once k_5 is known, one can calculate k_6 .

Alternate methods are discussed elsewhere for evaluating some of the rate constants in the above exciplex photokinetic scheme, but they appear to offer no real advantage over the direct approach outlined above.¹⁸

Once the constants $(k_1 + k_2)$, k_3 , k_4 and k_p have been determined, one can calculate the Stern-Volmer constant K_{SV}

$$K_{SV} = \left[\frac{I_m^0}{I_m} - 1 \right] \frac{1}{[Q]} = \frac{k_3 k_p}{(k_1 + k_2)(k_4 + k_p)} \quad (7)$$

and compare with experimental values derived from steady-state measurements. Discrepancies are interpreted^{19,20} in terms of failure of the assumption that $k_3 \neq f(t)$ or a failure of the kinetic scheme to describe the system in question.

Rate constants may then be determined as a function of temperature. When linear $\ln k_i$ vs $1/T$ plots are obtained, one can calculate

the parameters in the equation

$$k_i = A_i e^{-\Delta E_i^{\ddagger}/RT} \quad (8)$$

From the temperature coefficient of the ratio of k_3/k_4 , one obtains ΔH_C° , the enthalpy of the excited state equilibrium and from A_3 and A_4 one may obtain the entropies of activation of the forward and reverse reactions in the excited state equilibrium. Finally, from energy conservation (see Fig. 1)

$$h\nu(A \rightarrow A^*) = \Delta H_C^\circ + (h\nu_E)_{\max} + \Delta H_R \quad (9)$$

where $(h\nu_E)_{\max}$ is the maximum in the exciplex emission and ΔH_R is the repulsive potential energy in the Franck-Condon ground state at the equilibrium separation of A and Q in the exciplex. This yields ΔH_R .

It is emphasized that the rate constants k_3 , k_4 and k_p are obtained without recourse to steady-state data. It is only when one calculates k_1 , k_2 , k_5 and k_6 that it is necessary to use ϕ_M° and ϕ_E/ϕ_M , the latter ideally as a function of $[Q]$.

Likewise, one obtains ΔH_C° without recourse to the arguments of Stevens and Ban,²¹ i.e., if $k_4 \gg k_p$, then

$$\frac{\phi_E}{\phi_M} = \frac{k_3}{k_4} [Q] \quad (10)$$

If this is true, then of course one obtains ΔH_C° from $\ln \{\phi_E/(\phi_M[Q])\}$ vs $1/T$ at constant $[Q]$. As Selinger and McDonald²² point out, there are many cases where it is not clear that this is a valid approximation. One obviously needs individual rate parameters to establish ΔH_C° with certainty, unless one can measure ϕ_E/ϕ_M over so wide a temperature range that one sees the limiting behaviour for $k_4 \gg k_p$ as well as for $k_4 \ll k_p$. Finally, it is emphasized that K_{SV} is a function of k_3 , k_4 , k_5 and k_6 as well as $(\tau)_{Q=0}$. Changes in K_{SV} are clearly almost impossible to interpret unless one has values for the individual rate constants, since all are potentially functions of both temperature and solvent! K_{SV} is in fact not a particularly informative parameter except as a route to individual rate constants.

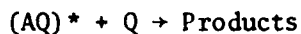
Some of the reasons for believing that the above model is realistic for many exciplex systems in non-polar or slightly polar solvents are as follows: (a) Two component fluorescence decay predicted by Eq. (1) is observed,^{18,19} along with the growth and decay predicted in Eq. (2). (b) Rate constants derived from transient luminescent measurement agree with steady-state measurements to the extent expected from the theory of diffusion controlled reactions.¹⁹

(c) The value for k_3 is reasonable - generally near but never above the diffusion control limit. (d) The observed variation of λ_1 and λ_2 with $[Q]$ can be reproduced by a single set of rate constants.

Thus, while one of course cannot rule out more complex schemes, we have found no need to invoke them to explain numerous experimental observations in non-polar or slightly polar solvents.

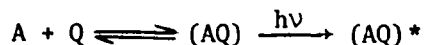
Extensive studies over the last 15 years by a number of groups indicate that the same general conclusion is valid in excimer systems.

The process



appears important only at high concentrations of quencher,²³ but most experimental studies have been below the quencher level where this is kinetically significant.

The complication represented by the process



is more difficult to rule out. While the exciplex is by definition repulsive in the ground state, some systems are certain to represent borderline cases of weak attraction. Such weak attraction causes the distribution of Q around A to be non-random. This alters the kinetics of the forward reaction (k_3), which are already complex due to the time evolution of concentration gradients.^{19,20} In addition, one must consider the photoselection of AQ pairs if one is using an exciting wavelength which favours AQ over A .

Unfortunately, one does not always see two components in the fluorescence decay of a fluorophor, even when the emission spectrum clearly indicates emission from both A^* and $(AQ)^*$. Measurements in the spectral region in which the decay is expected to be predominately due to the exciplex are frequently found to give similar if not identical decay curves as obtained from measurements of the decay of quenched A^* . In many cases, the decay is very close to a single exponential with a single decay constant λ , and frequently λ is found to be a strong function of $[Q]$. It is not unusual to find for such systems that λ follows the equation

$$\lambda = (\lambda_0 + B[Q]) / (1 + C[Q]) \quad (11)$$

If the following approximation is valid

$$\begin{aligned} & [(k_4 + k_3[Q])^2 + 2(k_4 - k_3[Q])(k_p - k_1 - k_2)]^{1/2} \\ & \approx k_4 + k_3[Q] + \frac{2(k_4 - k_3[Q])(k_p - k_1 - k_2)}{k_4 + k_3[Q]} \end{aligned} \quad (12)$$

Eq. (3) can be reduced to Eq. (11). This is related to the well known condition

$$k_4, k_3[Q] \gg k_1, k_2, k_p \quad (13)$$

to which must be added the more restrictive condition

$$k_4 + k_3[Q] > 2(k_4 - k_3[Q])(k_p - k_1 - k_2) \quad (14)$$

The conditions quoted in Eqs. 12 and 14 thus yield

$$\lambda = \frac{\lambda_0 + (k_3 k_p / k_4)[Q]}{1 + (k_3 / k_4)[Q]} \quad (15)$$

A plot of $(\lambda - \lambda_0)^{-1}$ vs $1/[Q]$ should yield a straight line with slope S given and intercept I given by

$$S^{-1} = (k_p - \lambda_0)(k_3/k_4) \quad (16)$$

$$I^{-1} = k_p - \lambda_0$$

This, $S/I = k_4/k_3$ and $I^{-1} + \lambda_0 = k_p$. The $[Q]$ dependence alone of λ (along with λ_0) fails to yield the complete set of rate constants, but rather yields only k_p and ratio k_3/k_4 . However, from the steady-state quenching measurements, we have

$$1/k_3 = 1/(k_q)_{ss} - k_4/k_3 k_p \quad (17)$$

where

$$(k_q)_{ss} = K_{SV}/\tau_0 \quad (18)$$

When this equation is used with values of k_3/k_4 and k_p , one can obtain k_3 . Then k_4 can be deduced. It is important to recognize that the success of this approach is the analysis of the so-called rapid equilibrium case depends critically upon being able to obtain a significant number from the subtraction of $(1/k_q)_{ss}$ and $k_4/k_3 k_p$. It is not uncommon that the two terms in Eq. (17) are nearly identical,

which causes the analysis to fail.

Figures 2, 3 and 4 illustrate experimental data consistent with Eqs. (15) and (16). The use of steady-state (Fig. 5) data with Eqs. (17) and (18) yielded individual rate constants.¹⁸ As will be discussed below, by varying the temperature, one can cause the cyanonaphthalene-olefin system to exhibit the classical two component decay. The rate constants obtained are consistent with those obtained in the rapid equilibrium region.¹⁸

3. EFFECT OF SOLVENT AND TEMPERATURE ON PHOTOKINETICS

Consider first α -cyanonaphthalene (CCN) quenched by 1,2-dimethyl cyclopentene (DMCP). When this system is examined in the vapour phase,²⁴ the quenching is observed to be very inefficient. One can estimate from lifetime measurements that the effective rate constant for quenching is about 10^{-3} of the gas kinetic limiting rate. One sees single exponential decay provided a buffer gas is present, but the system has thus far resisted attempts to recover rate constants.

If one now examines this same system in hexane,¹⁸ one finds that the observed photokinetic behaviour is a strong function of temperature. At room temperature and above, this system provides a classic example of the rapid equilibrium case. Eq. (15) is followed exactly and rate constants can be derived.¹⁸ The fluorescence decay follows a single exponential. If one now decreases the temperature at about 0° C, two component fluorescent decay becomes measurable (see Figs. 6 and 7) and rate constants can be obtained by the analysis described above. The agreement between calculated and observed values of λ_1 and λ_2 is shown in Figs. 8 and 9. These rate constants are consistent with those obtained from the analysis of the rapid equilibrium case.¹⁸ The temperature range of 40° to -40° C takes one from one limiting case to the other. The reason for this is that k_4 varies by three orders of magnitude over this temperature range. At a low temperature, the reverse reaction is slowed down and one can see two component decay, whereas at high temperature, the excited state quasi-equilibrium is the dominant kinetic process and the other processes merely bleed off excited species from this quasi-equilibrium. This is illustrated in Fig. 10.

Not only does k_4 control the photokinetic behaviour in non-polar solvents, but also, it rather than k_p , is the most solvent-sensitive rate constant in this system.²⁵ Merely changing the solvent from hexane to diethyl ether decreases k_4 at a given temperature by a factor of 20. If one uses a solvent such as THF, the photokinetics are now simply those of a diffusion controlled reaction. The solvent polarity has presumably reduced k_4 to the point where there is no significant reversibility, and individual rate constants cannot be recovered by nanosecond fluorometry.

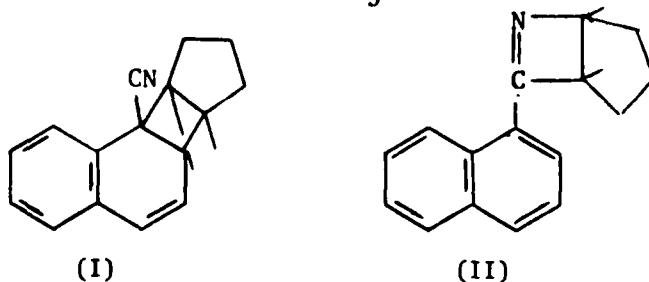
A study^{18,25} of the temperature coefficients of k_3 and k_4 revealed that ΔH_c° , the enthalpy change of the excited state reaction, is independent of the solvent change from hexane to ethyl acetate, as is ΔE_4^\ddagger , the activation energy for the reverse reaction. The dramatic drop in k_4 with solvent is thus due to the pre-exponential term and can be interpreted as an entropy of activation effect associated with changes in specific solvation by these two solvents of the highly dipolar exciplex.

k_4 also appears to depend upon the ionization potential of the donor when CCN is quenched by various olefins and a diene in hexane. As the ionization potential of the donor decreases, k_4 dramatically increases.¹⁸ This phenomenon deserves much more detailed study including the recovery of thermodynamic parameters for a number of donors.

k_p is also observed to decrease as one increases the solvent polarity. This is in part due to a drop in k_5 , but the largest contribution is a drop in k_6 .

Two products are observed by other laboratories²⁶⁻²⁸ for the reaction of excited CCN with DMCP. These are a ring adduct (I) and a nitrile adduct (II). Lewis and Hoyle²⁷ have in fact observed that nitrile addition is favoured in hexane and ring addition in ethyl acetate and that the quantum yield of each product decreases with increasing solvent polarity. This is consistent with our results for the variation of k_6 with solvent polarity if one assumes that k_6 is predominantly the product formation rate constant.

A similar trend is found in the k_5 values. k_5 , which was calculated with Eq. (5) on the assumption that k_1 , the CNN fluorescence probability, is temperature independent, decreases with increased solvent polarity. Owing to the problem of evaluating the contributions of various component configurations to the total exciplex wave function, a rigorous calculation of the radiative transition probability is not possible. However, the observed decrease in k_5 supports the opinion that the electronic structure of the complex changes as the solvent polarity is changed. k_5 is related to the transition



dipole moment, \vec{M}_E , for the exciplex through the equation²⁹

$$\vec{M}_E = \left| \frac{3hc^3 k_5}{64\pi^4 n v_\epsilon^3} \right|^{1/2} \quad (19)$$

\vec{M}_E in turn is given by

$$\vec{M}_E = \langle \psi_E | \vec{\mu}_{op} | \psi_G \rangle \quad (20)$$

in which $\vec{\mu}_{op}$ is the electric dipole moment operator, and ψ_E and ψ_G are given by

$$\psi_E = a_1 \psi_1(A^- D^+) + a_2 \psi_2(A^+ D^-) + a_3 \psi_3(A^* D) + a_4 \psi_4(AD^*) \quad (21)$$

$$\psi_G = \psi_0(AD) \quad (22)$$

Because the ground state is dissociative, it has been assumed for the present argument that charge-transfer contributions to its wave function are negligible. If the second and fourth terms in ψ_E are neglected, \vec{M} is given by

$$\vec{M}_E = a_1 \langle \psi(A^- D^+) | \vec{\mu}_{op} | \psi_0(AD) \rangle + a_3 \langle \psi_3(A^* D) | \vec{\mu}_{op} | \psi_0(AD) \rangle \quad (23)$$

The matrix element $\langle \psi(A^- D^+) | \vec{\mu}_{op} | \psi_0(AD) \rangle$ is approximately proportional to the overlap of the donor orbital in D and the acceptor orbital in A;²⁹ consequently, it is rather small and decreases with increasing intermolecular distance. As the exciplex becomes more ionic, a_3 decreases; thus, the dominating term in \vec{M}_E , $a_3 \langle \psi_3(A^* D) | \vec{\mu}_{op} | \psi_0(AD) \rangle$, decreases in more polar solvents. According to this analysis, therefore, both the increasing charge-transfer contribution, which reduces the second term in Eq. (23) and the probable increase in the intermolecular distance which reduces the first term, contribute to the decrease in k_5 with increasing solvent polarity.^{30,31}

Although k_5 decreases in the more polar solvents, the quantum yield of exciplex emission, ϕ_E , given by

$$\phi_E = \frac{k_5 k_3 [Q]}{k_o(k_4 + k_p) + k_p k_3 [Q]} \quad (24)$$

or, at infinite quencher concentration, by

$$\phi_E^\infty = \frac{k_5}{k_p} \quad (25)$$

increases. In general, in exciplexes, ϕ_E decreases with increasing solvent polarity;³² but an increased ϕ_E has also been observed in media of moderate dielectric constant.³³ Obviously, when increased solvent polarity induces an increase in k_p or a high probability for instantaneous radical ion production, with rate constant k_3' , ϕ_E will decrease. ϕ_E is then given by

$$\phi_E^\infty = \frac{k_5 k_3}{(k_3 + k_3')k_p + k_3' k_4} \quad (26)$$

However, the present results show that neither of these effects occurs for the CNN-DMCP system in the studied solvents. It is worthy of note that, in the present range of solvent polarity, both increases^{30,34-36} and decreases^{31,33} in k_p have been observed.

We have recently examined³⁷ the quenching of pyrene with N,N-dimethylaniline (DMA) substituted on the ring with tert-butyl groups. This work was suggested by the observation of Taylor et al.³⁸ that the Stern-Volmer constant for quenching strongly increases upon 3,5 di-tert butyl (DBDMA) substitution. The question then was: which rate constants in the expression

$$k_q = \frac{k_3 k_p}{k_4 + k_p} \quad (27)$$

were being influenced?

Detailed kinetic studies using the method of analysis described above conclusively demonstrate that the large increase in k_q for this system in non-polar solvents is due to a large decrease in k_4 . The forward reaction is diffusion controlled for both DMA and DBDMA quenchers. k_p decreased somewhat upon di-tert butyl substitution. These results point to the danger associated with interpretation of k_q . In this case, one has several remarkable effects occurring simultaneously. Di-tert butyl substitution increases the stability of the exciplex while altering the close sandwich pair configuration. Thus, there are both electronic and steric effects in operation and considerable information can be obtained from detailed kinetic studies as a function of solvent and temperature.³⁷ k_q alone tells one almost nothing!

The formation of exciplexes and excimers is almost always at the diffusion controlled limit. Thus, the formalism presented above, and almost universally used to analyze the photokinetics of these systems, is an approximation to the truth because in fact k_3 is a complex function of time. This subject has received detailed attention in another lecture by the author, but the subject requires some comment in the present context.

Mention must first be made of the studies of Eisenthal and co-workers.³⁹ They employed a mode-locked laser for picosecond excitation and were able by optical absorption to observe the growth of the exciplex between anthracene and diethylaniline in hexane. Their data fit the theory of diffusion controlled reactions quite well at the level of sophistication described by Smolochowski⁴⁰ including terms normally ignored, but important at short times.

Ware and Hui¹⁹ have also examined this problem by introducing an approximate time dependent for k_3 into the differential equations for the exciplex-excimer kinetic scheme, i.e.,

$$\frac{d[A^*]}{dt} = k_4[AQ^*] - [k_1 + k_2 + k_3(t)[Q]][A^*]$$

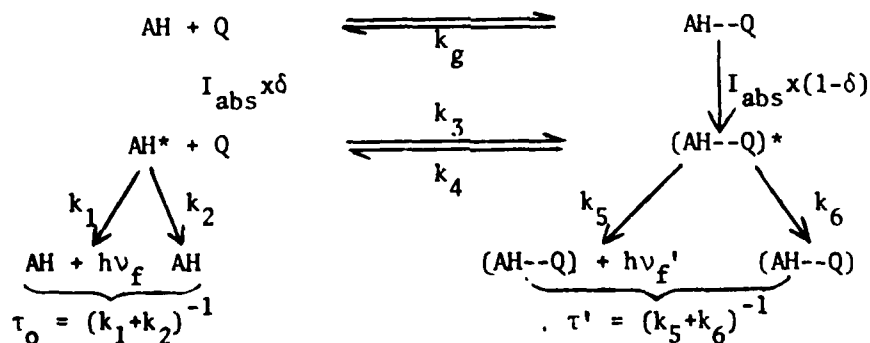
$$\frac{d[AQ^*]}{dt} = k_3(t)[Q][A^*] - [k_4 + k_5 + k_6][AQ^*]$$

This system of equations was then solved by numerical integration. It was found that distortions to the leading edge of both the exciplex growth curve and the monomer decay curve were caused by the time dependence of k_3 .

However, if deconvolution was carried out only over those portions of the decay curves where $k_3(t)$ had reached its limiting time independent value, the problem could be avoided.¹⁹

4. FLUORESCENCE QUENCHING VIA H-BOND FORMATION

The techniques described above are readily applicable to the quenching of excited species by H-bond formation. However, one frequently has the added complication of a bound ground state complex which competes with A^* for the incident radiation. The photokinetic scheme can now be depicted by



A number of years ago, the author published⁴¹ an account of the behaviour of such a system where $k_3 \gg k_4$. Recently, Dr. M. Martin and

and the author have completed a study⁴² in this laboratory of a more difficult system, carbazole quenched by pyridine and substituted pyridines. This system exhibits weak fluorescence from the excited H-bond complex. Steady-state analysis of the above scheme yields

$$\frac{\phi}{\phi_0} = \frac{\delta + \frac{k_4\tau'(1-\delta)}{1+k_4\tau'} + \frac{k_5\tau'(1-\delta)}{k_1\tau_0(1+k_4\tau')}}{1 + \left(\frac{\tau_0 k_3}{1+\tau'k_4}\right)[Q]} + \frac{\left\{ \frac{k_5\tau'k_3\left(\delta + \frac{k_4\tau'(1-\delta)}{1+k_4\tau'}\right)}{k_1(1+k_4\tau')} + \frac{k_3k_5\tau'(1-\delta)}{k_1(1+k_4\tau')^2} \right\} [Q]}{1 + \left(\frac{\tau_0 k_3}{1+\tau'k_4}\right)[Q]} \quad (28)$$

whereas the transient behaviour is given by modifications of Eqs. (1) and (2), provided the excitation is almost entirely to A* for the lifetime measurements. In this system, the absorption due to the ground state complex is somewhat separated from that of the carbazole. Our kinetic studies have resulted in the following conclusions:

(a) The kinetic model given above appears valid. Rate constants derived from the kinetics by transient measurements, when introduced into Eq. (28), yield excellent fits such as that illustrated in Figs. 11 and 12. The only adjustable parameter is the excited state complex lifetime τ' which is found by an iterative procedure. For the carbazole-pyridine excited complex, we obtain a lifetime of 52 psec. Thus, there are very rapid radiationless processes in this excited state complex which probably yield the ground state molecule.⁴³ No photochemistry or proton transfer is observed.

(b) The effect of methyl and phenyl substitution on the pyridine has also been studied and leads to the conclusion that the coplanarity of the carbazole and pyridine ring systems is not significant in determining the quenching probability.

(c) The deuteration of the amine hydrogen of the carbazole also produces no change in the photophysical behaviour, which suggests that N-H Franck-Condon overlap is not involved in determining the radiationless process in this excited complex. Thus, the notion⁴³ that quenching involves a delocalization type interaction between the π systems of the carbazole and pyridine is probably not correct.

5. OTHER TOPICS

Time and space limitations obviously make it impossible to deal with all aspects of excimer-exciplex photophysics. The emphasis in this work has been on the determination of rate constants by pulse fluorometry and steady-state fluorescence spectroscopy and relative steady-state intensity measurements.

For more information, the reader should consult the reviews by Mataga and Ottolenghi,¹⁶ Davidson,⁹ Ware,⁴⁴ Stevens,⁴⁵ Birks,⁴⁶ Ware and Gordon,⁴⁷ Beens and Weller,⁶ as well as the classical works of Birks⁴⁸ and Mataga and Kubota.⁴³

Examination of these reviews will reveal the great impact of laser spectroscopic techniques in this field as an approach to understanding the structure of the excimer and exciplex which compliments pulse fluorometry studies.

6. CONCLUSIONS

The molecular complex stable in its ground electronic state has been studied extensively over the past several decades and while there are many unanswered questions, the properties and behaviour of such species is reasonably well understood. The exciplex offers a much greater challenge. One cannot study its physical and chemical properties at one's leisure. It cannot be crystallized and subjected to x-ray analysis. One must depend upon indirect observations, the interpretation of which is rarely straightforward. It is reasonable to expect that as we learn more about the physical and chemical properties of the exciplex, we will see many more applications of this particular electron donor-acceptor phenomenon. One, however, should not underestimate the time required to collect quantitative kinetic and thermodynamic data. To study a single system as a function of solvent, temperature and concentration of quencher requires one half of a man year, provided there are no unexpected problems and the system is "cooperative". If one so wishes to study in this detail a whole set of donors and acceptors, the magnitude of the task is somewhat frightening as well as expensive. Add to this studies of photochemical products and laser flash photolysis studies of transient spectra, and one may begin to visualize the magnitude of the exciplex problem. Finally, all the work should be done in four or five solvents.

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Figure 1. Schematic potential energy diagram for exciplex formation. E_{0-0} : A* Q-0 molecular fluorescence energy; ΔH° : exciplex binding energy; $h\nu_E$: energy of exciplex fluorescence maximum; E_R : ground state repulsion energy.

Figure 2. Typical exciplex fluorescence decay curves for α -cyanonaphthalene unquenched and quenched 1,2-dimethylcyclopentene in hexane at 25°.

Figure 3. Exciplex fluorescence decay constant in hexane as a function of 1,2-dimethylcyclopentene concentration. Points, experimental. Lines, best fit using Eq. (25).

Figure 4. Linearization of the curves shown in Fig. 3.

Figure 5. Steady-state Stern-Volmer plots for α -cyanonaphthalene quenched by 1,2-dimethylcyclopentene in hexane.

Figure 6. Typical monomer decay curve: α -cyanonaphthalene + dimethylcyclopentene-1,2 (2.85×10^{-2} M) at -31° C.

Figure 7. Typical exciplex decay curve: α -cyanonaphthalene + dimethylcyclopentene-1,2 (1.92×10^{-2} M) at -40° C.

Figure 8. Comparison of experimental and calculated λ_1 .

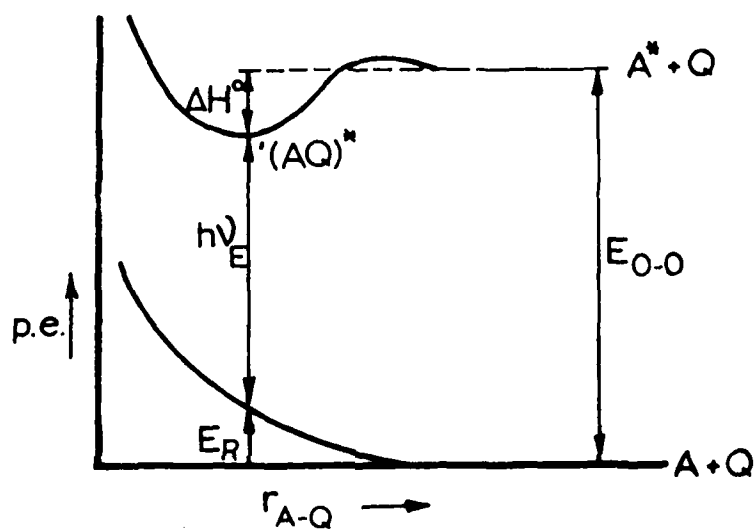
Figure 9. Comparison of experimental and calculated λ_2 .

Figure 10. Arrhenius plots of k_3 , k_4 , k_p . Open circle values were taken from paper I.

Figure 11. Best fit obtained between experimental and calculated data for the change in the total carbazole fluorescence yield (free and bonded carbazole), with increasing quencher concentration, in oxygen-free solution: (●) Q = pyridine; (○) Q = 2,6-DMP.

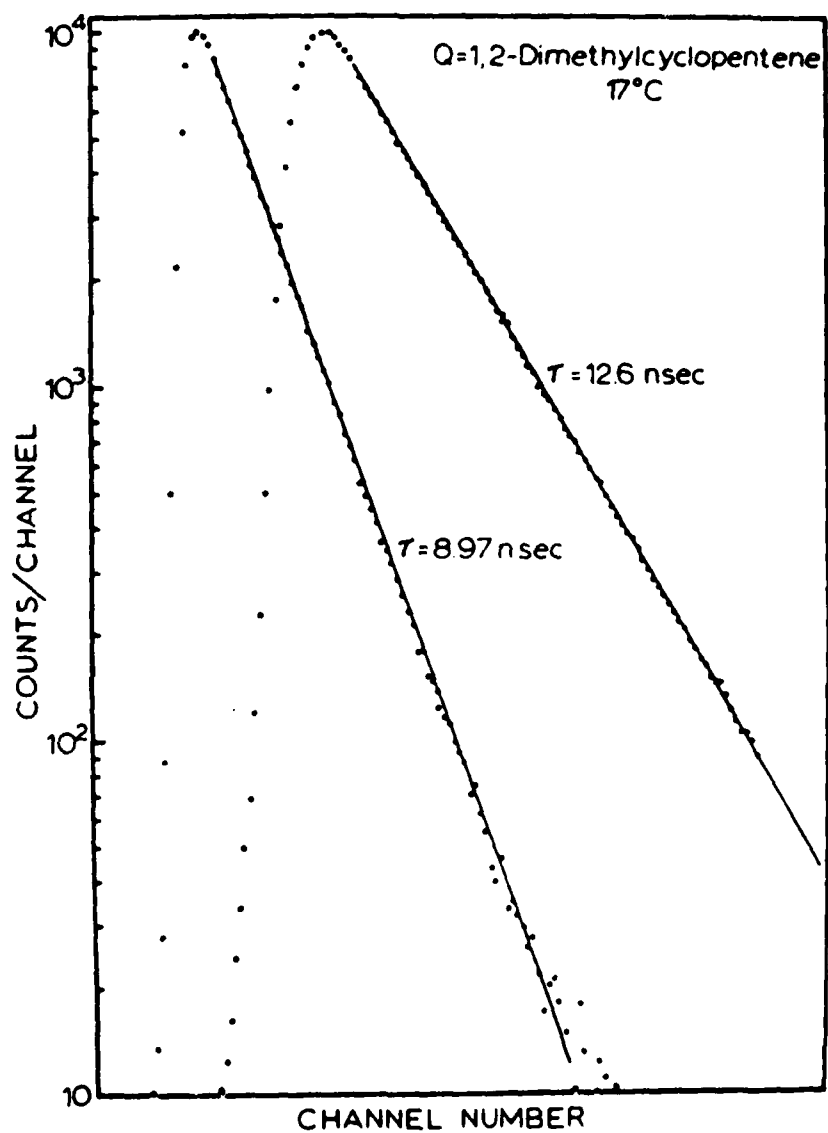
Figure 12. Best fit obtained between experimental and calculated data for the change in the total carbazole fluorescence yield (free and bonded carbazole), with increasing quencher concentration, in air-saturated solution: (■) Q = pyridine; (□) Q = 2,6-DMP.

KINETIC ASPECTS OF EXCIPLEX PHOTOPHYSICS



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KINETIC ASPECTS OF EXCIPLEX PHOTOPHYSICS



KINETIC ASPECTS OF EXCIPLEX PHOTOPHYSICS

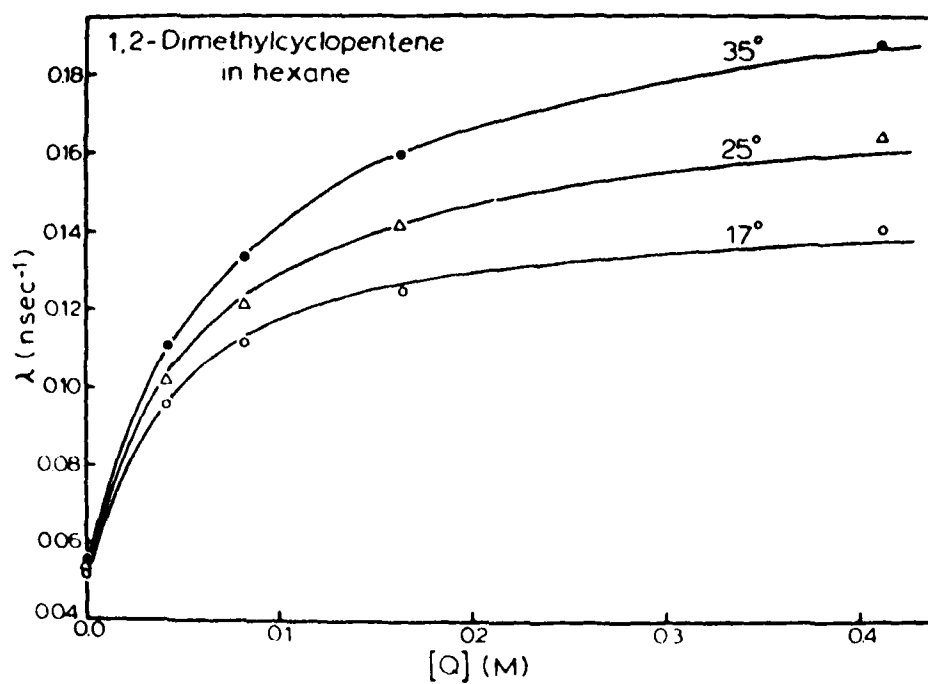


Fig. 3

KINETIC ASPECTS OF EXCIPLEX PHOTOPHYSICS

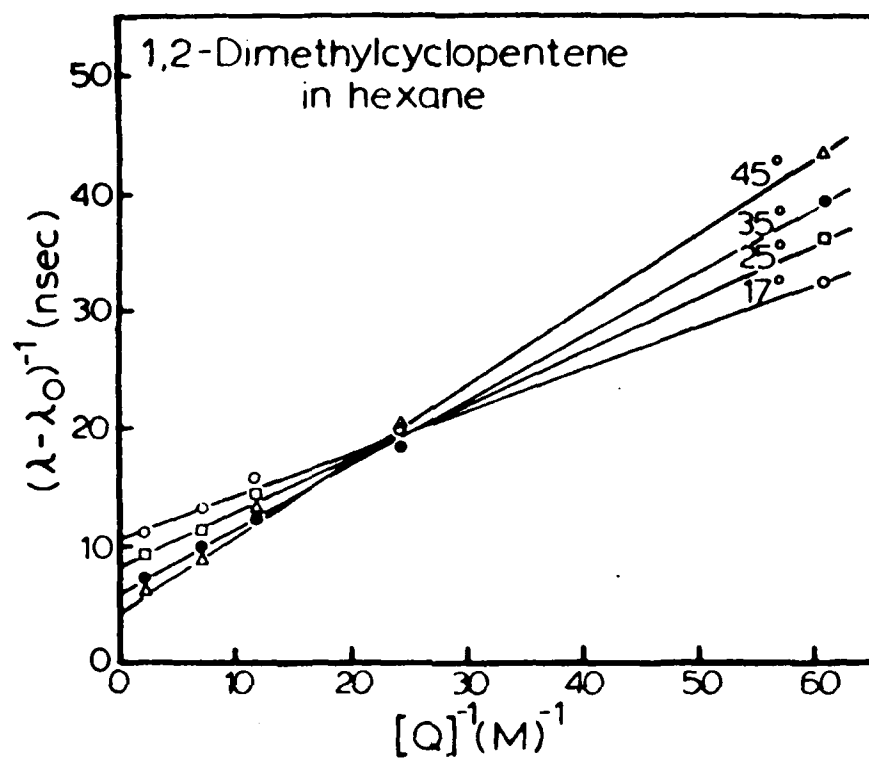
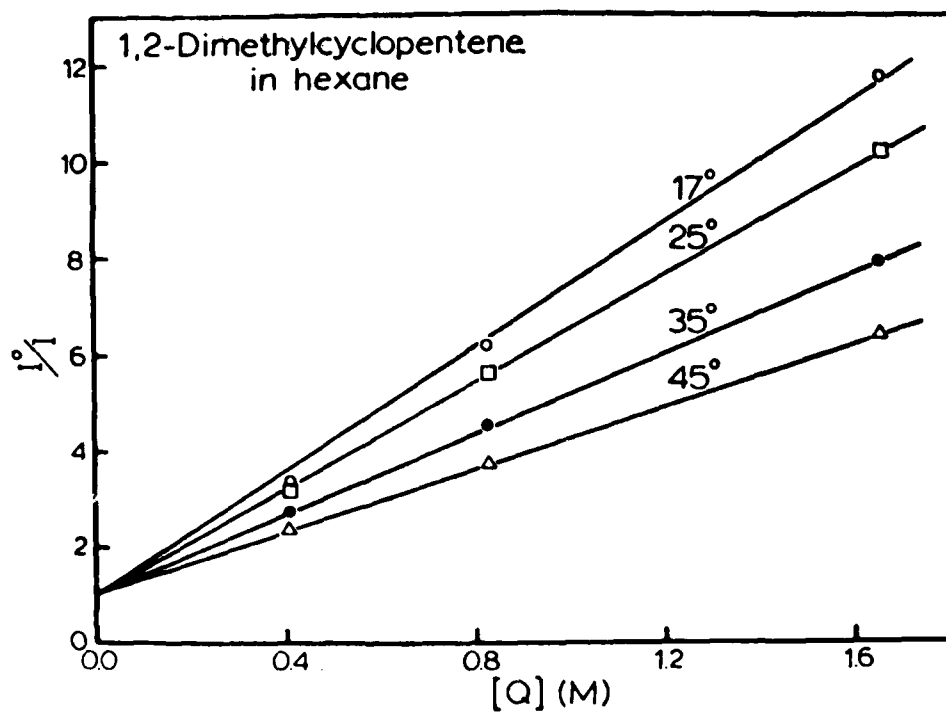


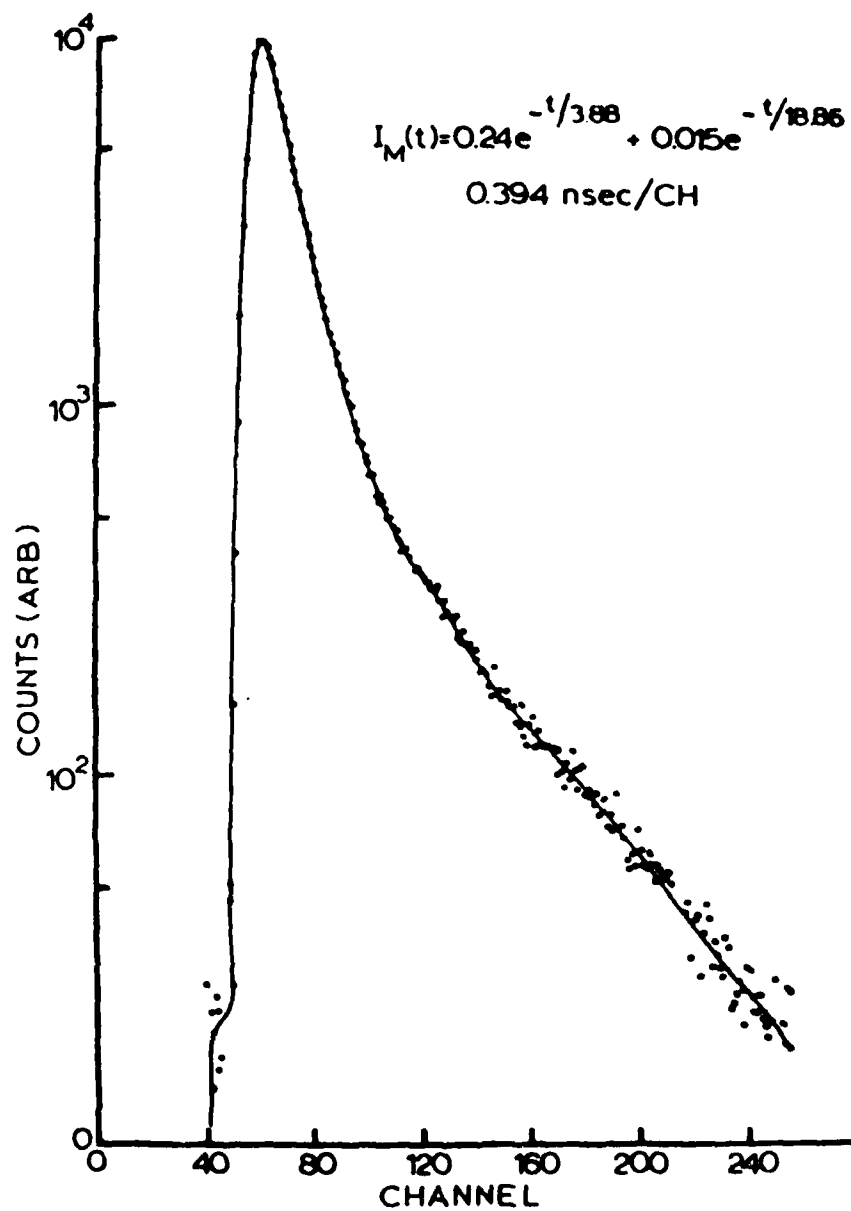
FIG. 4

KINETIC ASPECTS OF EXCIPLEX PHOTOPHYSICS



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KINETIC ASPECTS OF EXCIPLEX PHOTOPHYSICS



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KINETIC ASPECTS OF EXCIPLEX PHOTOPHYSICS

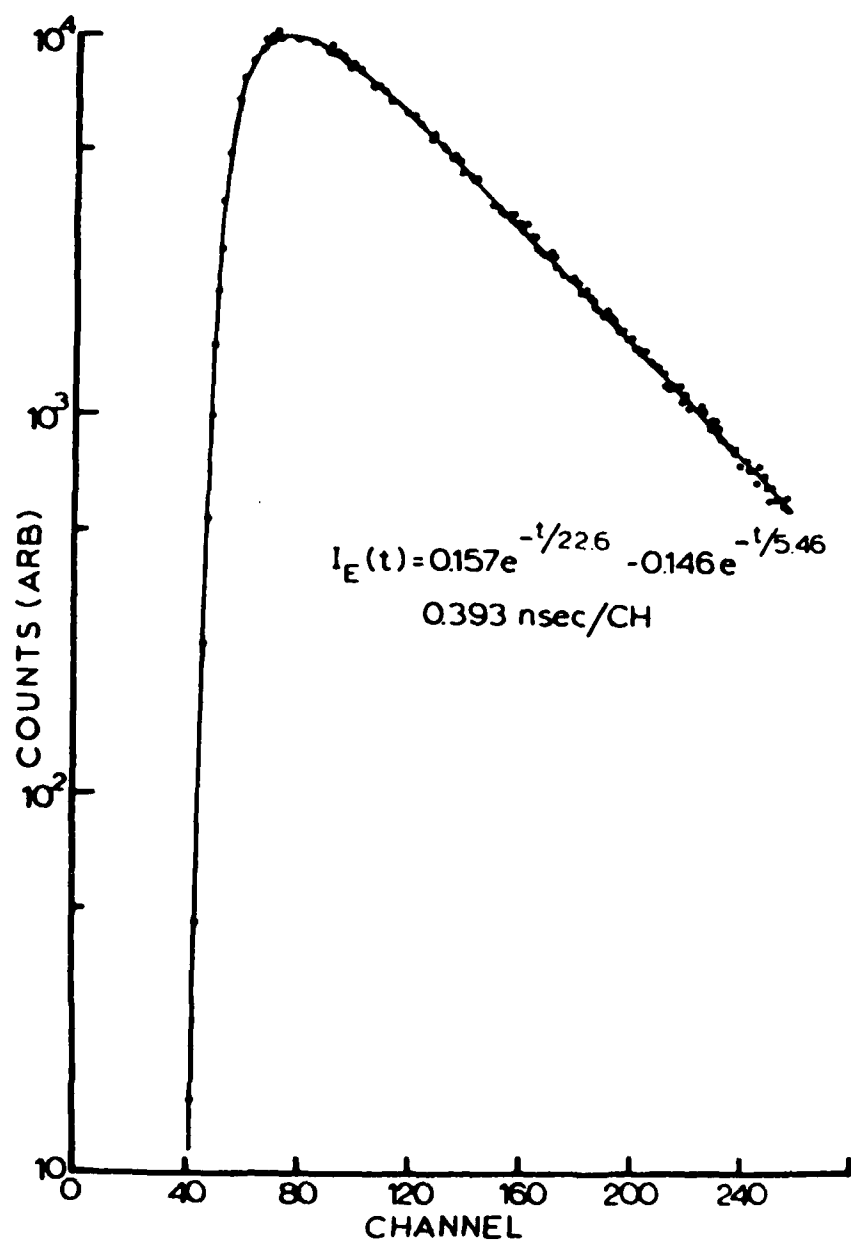
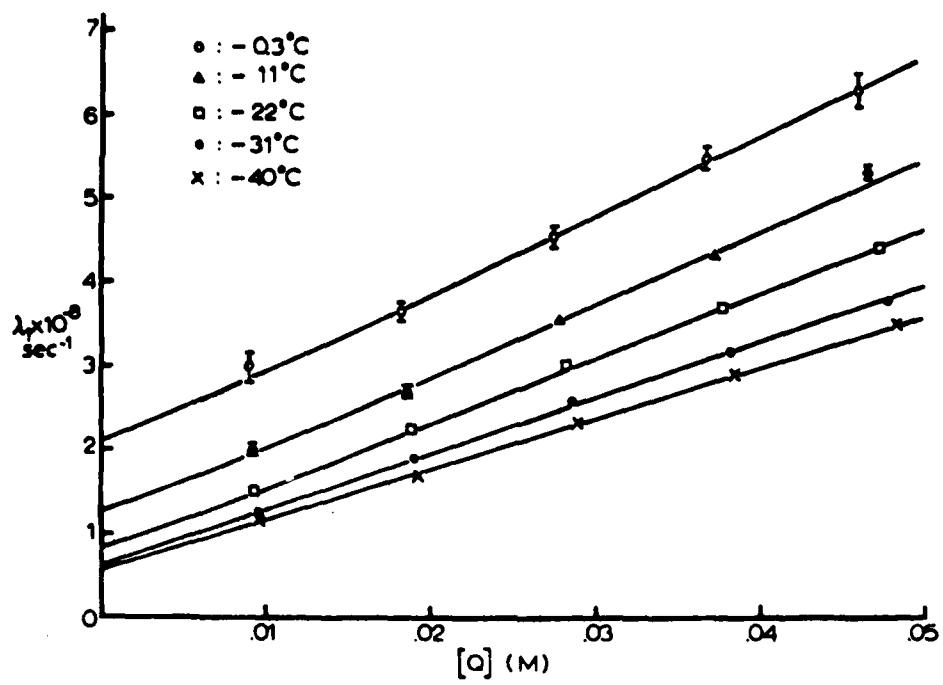


FIG 7

KINETIC ASPECTS OF EXCIPLEX PHOTOPHYSICS



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KINETIC ASPECTS OF EXCIPLEX PHOTOPHYSICS

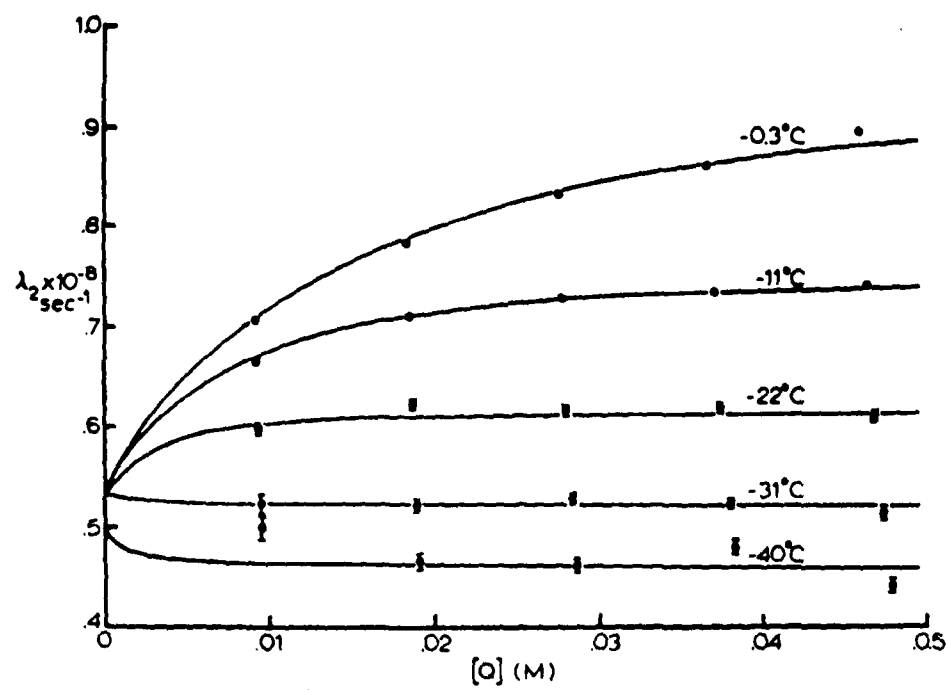
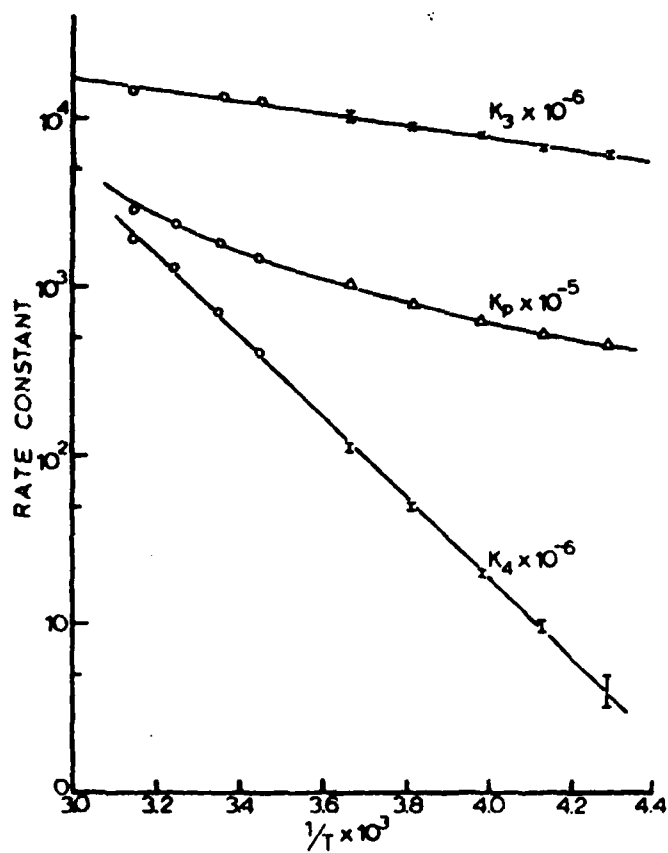


FIG 9

KINETIC ASPECTS OF EXCIPLEX PHOTOPHYSICS



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KINETIC ASPECTS OF EXCIPLEX PHOTOPHYSICS

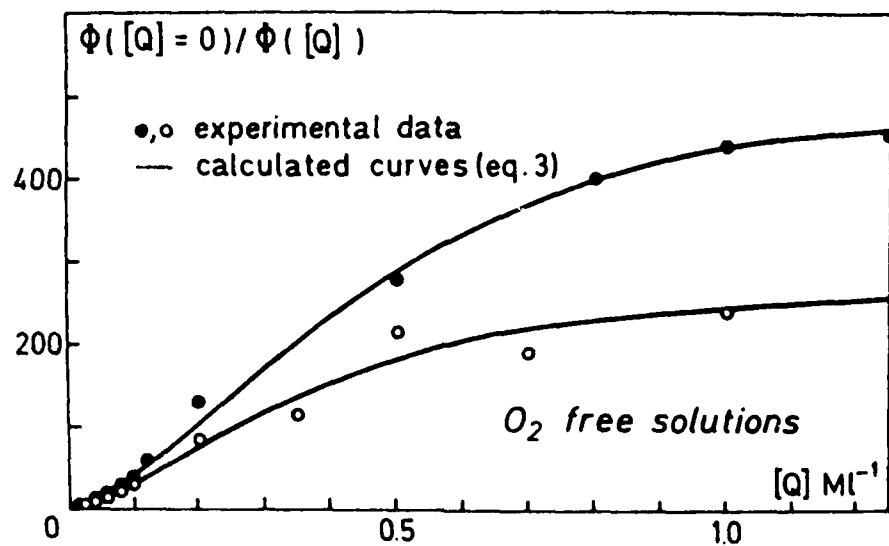


FIG. 11

KINETIC ASPECTS OF EXCIPLEX PHOTOPHYSICS

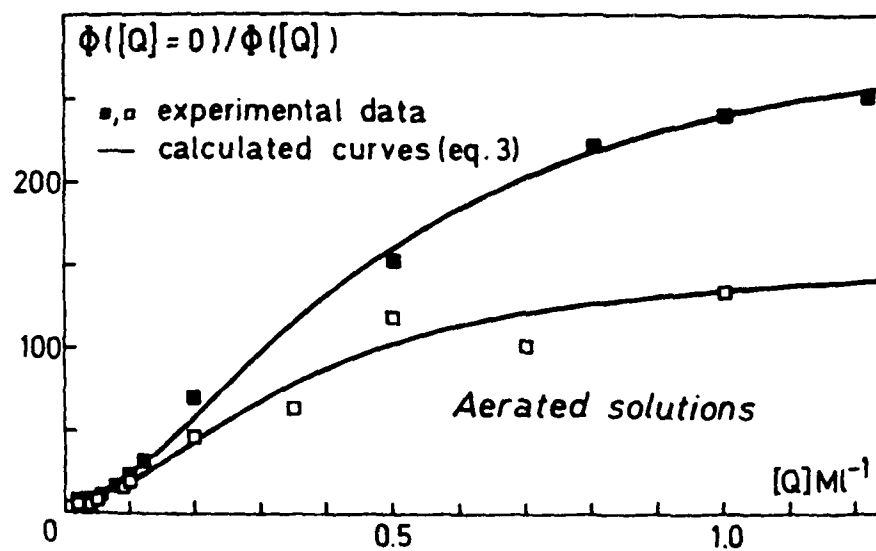


FIG. 12